

	Type	L #	Hits	Search Text	DBs
1	BRS	L1	1	US-6086832-\$.DID.	USPAT
2	BRS	L2	1	"20020081254"	US- PGPUB
3	BRS	L3	0	US-5779995-\$.DID.	US- PGPUB
4	BRS	L4	1	US-5779995-\$.DID.	US- PGPUB; USPAT
5	BRS	L5	130606	hydrogenation	US- PGPUB; USPAT; USOCR; EPO; JPO; DERWEN T
6	BRS	L6	6493	15 and tank	US- PGPUB; USPAT; USOCR; EPO; JPO; DERWEN T
7	BRS	L7	154415	16 anfd baffle	US- PGPUB; USPAT; USOCR; EPO; JPO; DERWEN T

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8	BRS	L8	248	16 and baffle	US- PGPUB; USPAT; USOCR; EPO; JPO; DERWEN T
9	BRS	L9	195	18 and catalyst	US- PGPUB; USPAT; USOCR; EPO; JPO; DERWEN T
10	BRS	L10	65	19 and (agitator or stirrer)	US- PGPUB; USPAT; USOCR; EPO; JPO; DERWEN T

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US005779995A

**United States Patent** [19][11] Patent Number: **5,779,995**

Witt et al.

[45] Date of Patent: **Jul. 14, 1998**

[54] **SLUDGE PHASE REACTOR AND PROCESS  
FOR PERFORMING SLUDGE PHASE  
REACTIONS**

[52] U.S. Cl. .... **422/215; 422/224; 422/225;  
422/227**

[58] Field of Search ..... **422/215, 225,  
422/224, 227**

[75] Inventors: **Harro Witt, Kuden; Uwe Jens  
Zarnack, Brunsbüttel; Helko  
Beckhaus, Leverkusen, all of Germany**

[56] **References Cited**

**U.S. PATENT DOCUMENTS**

3,761,521 9/1973 Alberitieri et al. .... 260/580  
4,882,283 11/1989 Gentry ..... 435/316  
5,563,296 10/1996 Zarnack et al. .... 564/422

*Primary Examiner*—Nina Bhat

*Attorney, Agent, or Firm*—Joseph C. Gil; Noland J. Cheung

[73] Assignee: **Bayer Aktiengesellschaft, Leverkusen,  
Germany**

[21] Appl. No.: **809,840**

[22] PCT Filed: **Sep. 25, 1995**

[86] PCT No.: **PCT/EP95/03786**

§ 371 Date: **Apr. 2, 1997**

§ 102(e) Date: **Apr. 2, 1997**

[87] PCT Pub. No.: **WO96/11052**

PCT Pub. Date: **Apr. 18, 1996**

[30] **Foreign Application Priority Data**

Oct. 7, 1994 [DE] Germany ..... 44 35 839.3

[51] Int. Cl.<sup>6</sup> ..... **B01J 8/22; B01J 19/00**

[57] **ABSTRACT**

A reactor is described for exothermic sludge phase reactions which comprises as the heat exchanger an annular chamber which is covered at the top and the bottom by the reaction mass in the reactor, the annular chamber comprising a plurality of vertical passage ducts having a circular cross-section for the reaction mass, and the coolant flowing through the annular chamber between the passage ducts for the reaction mass.

**4 Claims, 2 Drawing Sheets**

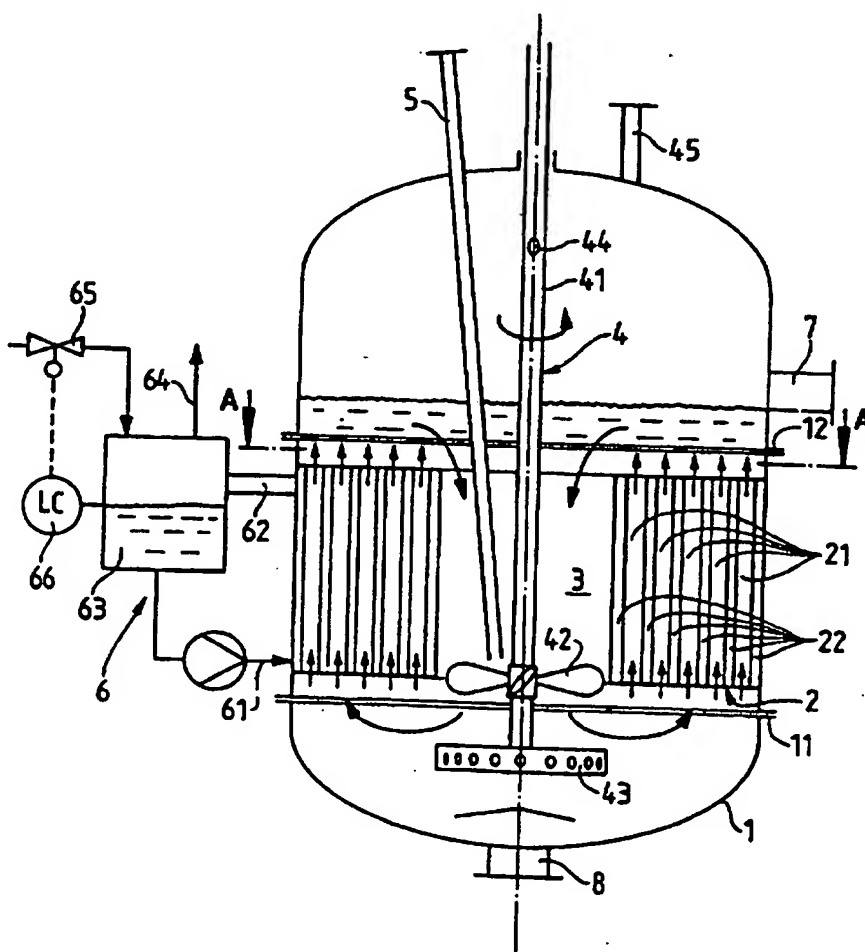
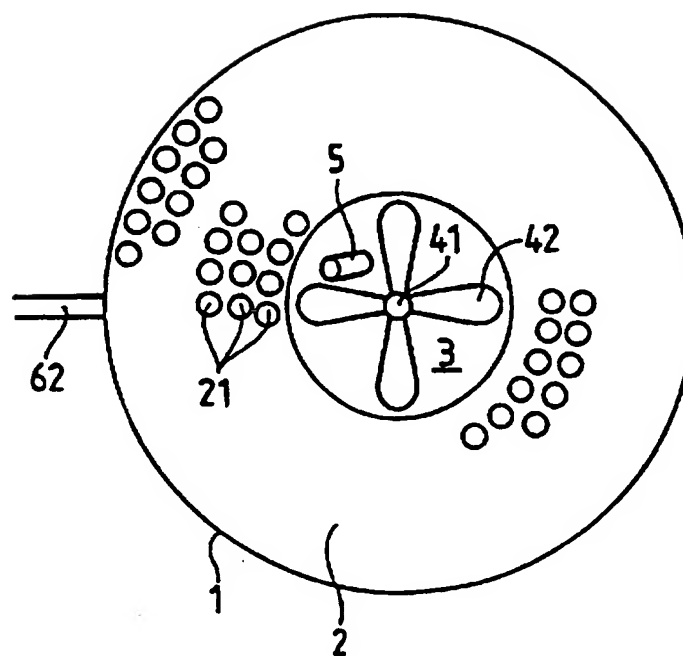




Fig. 2



## SLUDGE PHASE REACTOR AND PROCESS FOR PERFORMING SLUDGE PHASE REACTIONS

This continuation-in-part application, which is designated for filing in the United States, corresponds to PCT Application number PCT/EP 95/03786, which was filed on Sep. 25, 1995 and claims priority over DE Application No. P 44 35 839.3, which was filed on Oct. 7, 1994.

### BACKGROUND OF THE INVENTION

Sludge phase reactions are reactions in which at least one finely divided solid phase and one fluid phase participate.

Highly exothermic sludge phase reactions require effective discharge of the heat of reaction. Sludge phase reactors therefore thus generally include expensive heat exchanger constructions inside the reaction container (see, e.g., U.S. Pat. No. 3,243,268 or European patent 263,935). In the case of the known sludge phase reactors, the heat exchange is brought about as a result of the fact that the reaction mass is pumped around so-called "field" heat exchanger pipes or boiler pipes which are closed at one end and in which the heat-transfer medium and the resultant steam are guided counter-currently. The disadvantage of this type of heat exchange is the flow speed of the reaction mass which differs in relation to the reactor chamber and the low degree of efficiency of the heat exchanger brought about thereby. The different flow speed of the reaction mass gives rise to areas in which the flow is substantially decreased and the solid components involved in the reaction can be deposited.

### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a cross-section through the sludge phase reactor according to the invention; and

FIG. 2 shows is a cross-sectional view of the reactor of FIG. 1 in the direction of A—A of FIG. 1.

### DESCRIPTION OF THE INVENTION

In accordance with the invention it is now proposed to provide as a heat exchanger a container through which the heat-transfer medium essentially flows in one direction only, the container being equipped with a plurality of passage ducts having a circular cross-section for the reaction mass. In accordance with the invention the reaction mass is consequently guided "inversely" in the heat exchanger in comparison with conventional evaporation-heat exchangers.

The subject matter of the present invention is a sludge phase reactor for exothermic sludge phase reactions, comprising the following components:

- a) a reaction container;
- b) a heat exchanger in the form of an annular chamber through which the coolant and the reaction mass flow inside the reaction container, the annular chamber being covered at the top and bottom by the reaction mass;
- c) a central free flow chamber inside the annular chamber for the return flow of the reaction mass;
- d) a central agitator which circulates the reaction mass between the central free flow chamber and the annular chamber;

wherein the annular chamber comprises a plurality of vertical passage ducts having a circular cross-section for the reaction mass, and the coolant flows through the annular chamber between the passage ducts for the reaction mass.

Preferably reaction mass and heat-transfer medium flow through the heat exchanger annular chamber substantially in the same direction. In particular the passage ducts for the reaction mass through the annular chamber are flowed through vertically upwards. In this case the agitator is preferably disposed at the lower outlet of the central free flow chamber. At least one of the reaction components is delivered in the immediate vicinity of the agitator such that firstly the reaction component is rapidly distributed in the reaction mass and secondly the delivered reaction component with the reaction mass is introduced very rapidly into the heat exchanger.

In order for the reaction to be performed continuously, an overflow from which reacted reaction mass can be continuously drawn off is provided above the fluid level in the reaction container.

Preferably a substance which evaporates at the reaction temperature and which is delivered in liquid form at the base of the heat exchanger annular chamber and is drawn off in gaseous form from the head of the heat exchanger annular chamber is used as the heat-transfer medium. Particularly preferably, water is used as the heat-transfer medium and the heat exchange takes place with the production of steam. The coolant temperature is preferably set by maintaining the pressure of the steam produced.

Preferably reactions involving a gas phase are performed in the sludge phase reactor according to the invention. To this end the agitator is in the form of a gassing agitator or comprises an additional gassing component.

The sludge phase reactor according to the invention and having a gassing agitator is particularly suitable for performing the sludge phase hydrogenation of aromatic nitro compounds, particularly preferably for the hydrogenation of dinitrotoluenes with the production of the corresponding diamines.

The invention will be explained in greater detail with reference to the attached drawings.

The reactor according to FIG. 1 comprises a reaction container 1 which is constructed from three parts which are flanged together by means of flanges 11 and 12. The central part of the reaction container 1 contains the annular heat exchanger 2 which comprises an annular chamber closed on all sides and is penetrated by a plurality of passage pipes 21 through which the reaction mass flows rising in the direction indicated by the arrows. Located in the remaining space 22 of the annular chamber 2 is the heat-exchanger medium. As indicated by arrows, the return flow of the reaction mass is through the central free flow chamber 3 inside the annular heat exchanger 2. The circulating flow of the reaction mass is brought about by the agitator 4 with a central agitator shaft 41, driven externally of the reactor, and an agitator blade 42. In this respect the agitator blade 42 is disposed at the bottom, at the level of the outlet from the central flow chamber 3. In the embodiment illustrated the agitator shaft 41 is in the form of a hollow shaft and comprises a gassing device 43 below the agitator blade 42. The gas for gassing the reaction mass is drawn out of the gas chamber in the upper part of the reaction container 1 by means of intake openings 44 in the agitator shaft 41. A predetermined gas pressure is ensured via the gas delivery connection 45. When the reactor according to the invention is used as preferred for hydrogenating aromatic nitro compounds, hydrogen is used at a pressure of between 10 and 40 bar. More advantageously, fresh hydrogen can be delivered directly into the reaction mass. The aromatic nitro compound is introduced via delivery line 5 into the immediate vicinity of the agitator blade 42. Precious metals or nickel for example on carrier particles such as



3

carbon,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and the like or Raney-nickel catalysts are dispersed in the reaction mass as the finely divided solid phase. The product is continuously drawn off at the overflow 7 so that a constant fluid level is maintained. The heat exchanger annular chamber is further supplied from a heat exchanger medium circuit 6. The heat exchanger medium, preferably water just below boiling point, is introduced into the bottom of the heat exchanger at 61. Steam emerges from the top of the heat exchanger at 62 and is delivered to the steam separator 63. The arrow 64 indicates the discharge of the steam for the recovery of energy. The cooling water inflow valve 65 is controlled by means of a level regulating device 66 for the water level in the steam separator 63. When the reactor according to the invention is used as preferred for hydrogenating aromatic nitro compounds, the coolant pressure 64 is regulated so that a temperature of 120° to 250° C. is maintained in the reactor.

The numerals in FIG. 2 designate the same components as in FIG. 1. Only some of the passage pipes 21 are shown. The heat exchanger 2 can comprise between 100 and 3000 passage pipes 21 depending on the nominal width of the pipes (25–10 mm) and the diameter of the heat exchanger (up to 3 m).

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

What is claimed is:

1. A sludge phase reactor for exothermic sludge phase reactions comprising:

(a) a reaction container;

4

(b) a heat exchanger disposed within said reaction container, said heat exchanger in the form of an annular chamber through which heat-exchanging medium and reaction mass flow;

(c) wherein said annular chamber comprises a plurality of open-ended vertical passage ducts having a circular cross-section for said reaction mass, and wherein said heat-exchanging medium flows through said annular chamber between said passage ducts for said reaction mass;

(d) a central free flow chamber inside the annular chamber for the return flow of the reaction mass;

(e) a central agitator which circulates the reaction mass between the central free flow chamber and the annular chamber;

(f) wherein said agitator is additionally in the form of a gassing agitator; and

(g) wherein said agitator conveys said reaction mass downwards in said central flow chamber and produces an upward flow in said vertical passage ducts.

2. The sludge phase reactor of claim 1, wherein the agitator is disposed at the outlet of the central free flow chamber and is formed with accessible walls.

3. The sludge phase reactor of claim 1, wherein at least one reacting agent is introduced into the reaction mass in the immediate vicinity of the agitator.

4. A sludge phase reactor according to claim 1, wherein said heat exchanging medium and said reaction mass flow through said annular chamber in substantially the same direction.

\* \* \* \* \*



US 20020081254A1

(19) **United States**

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**Boger** (43) **Pub. Date: Jun. 27, 2002**

(54) **MONOLITH LOOP REACTORS**

(52) **U.S. Cl.** ..... **422/222; 422/224; 422/231;**  
**422/211**

(76) **Inventor: Thorsten R. Boger, Idstein-Walsdorf**  
**(DE)**

**Correspondence Address:**  
**CORNING INCORPORATED**  
**SP-TI-3-1**  
**CORNING, NY 14831**

(57) **ABSTRACT**

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(22) **Filed: Dec. 21, 2000**

**Publication Classification**

(51) **Int. Cl.<sup>7</sup> ..... B01J 8/02**

An improved recirculating tank reactor incorporating the advantages of a fixed catalyst includes a monolithic honeycomb catalyst positioned within the tank in such a manner so as to provide an adjacent bypass passageway. Internal flow activation means are provided for recirculating the reactant liquid within the tank in such a manner that it sequentially flows through channels in the catalyzed honeycomb substrate and around the substrate through the bypass passageway.

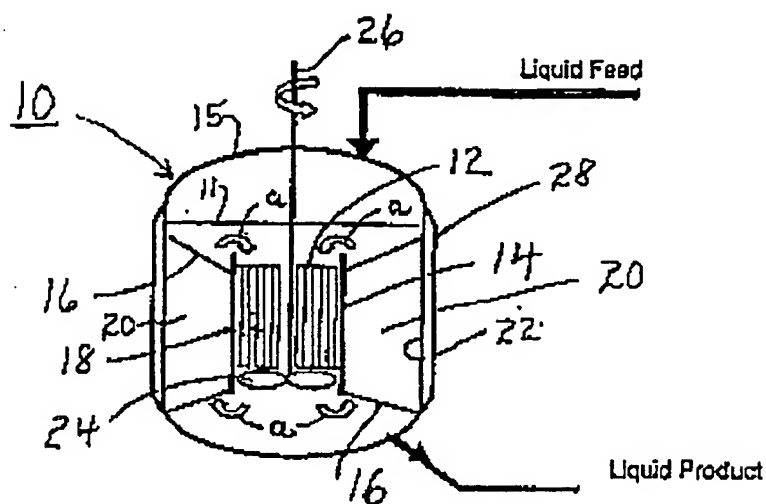


FIG. 1

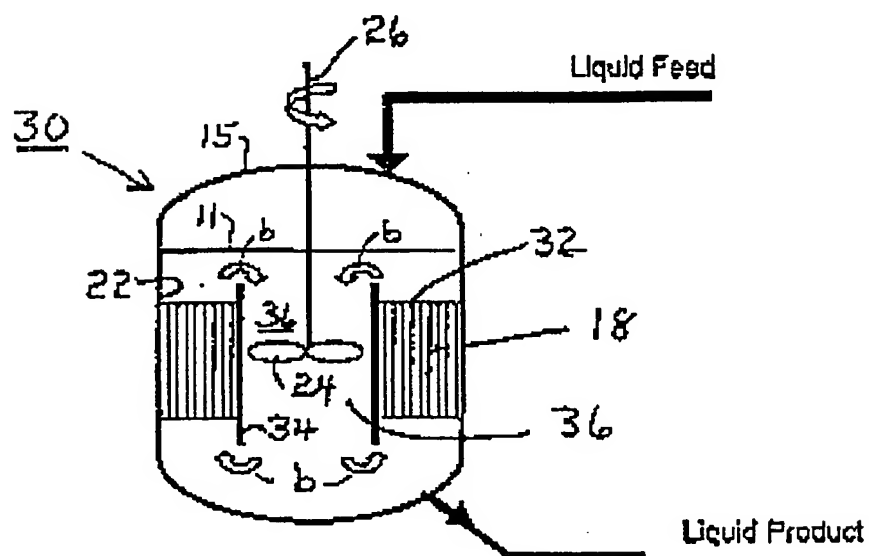


FIG. 2

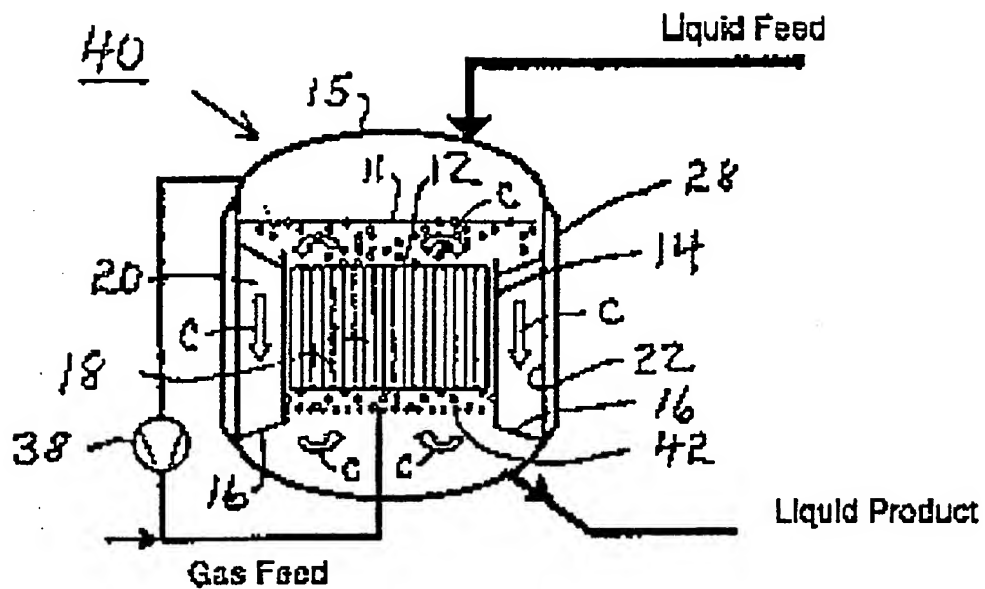


FIG. 3

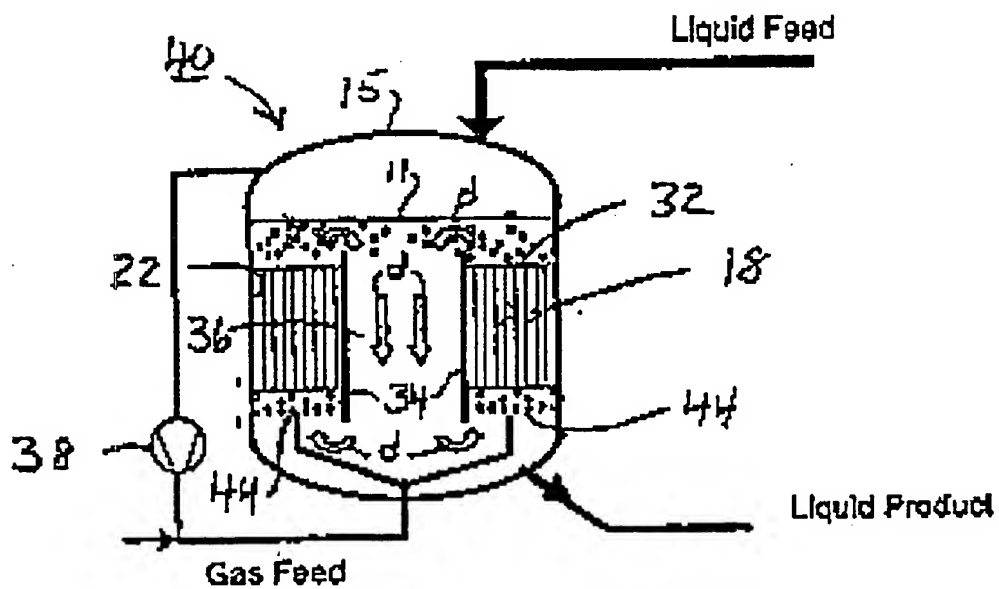


FIG. 4

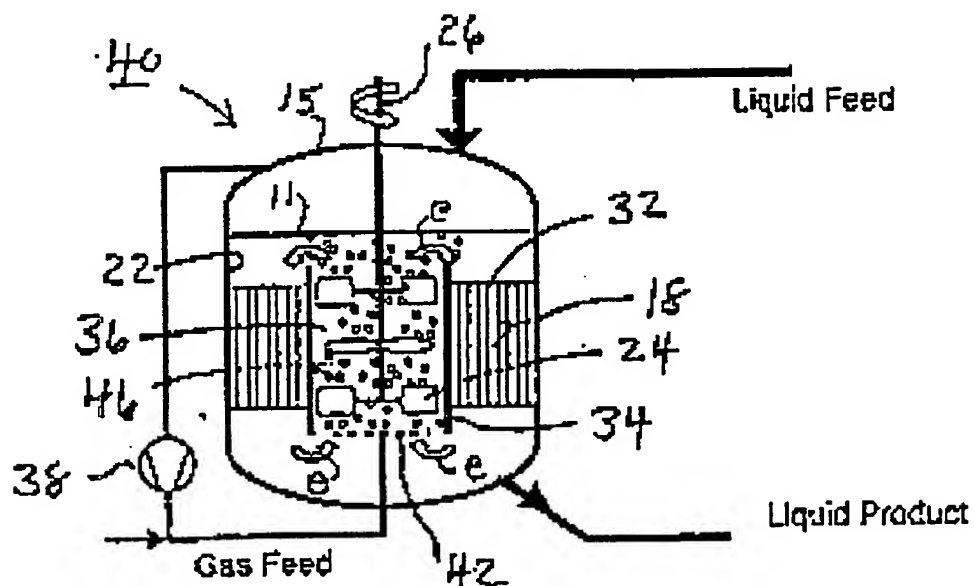


FIG. 5

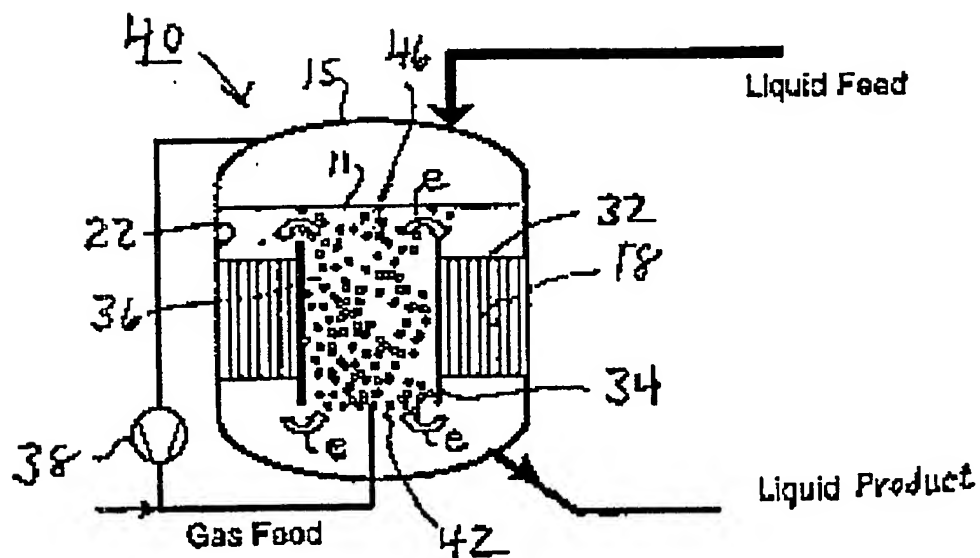


FIG. 6

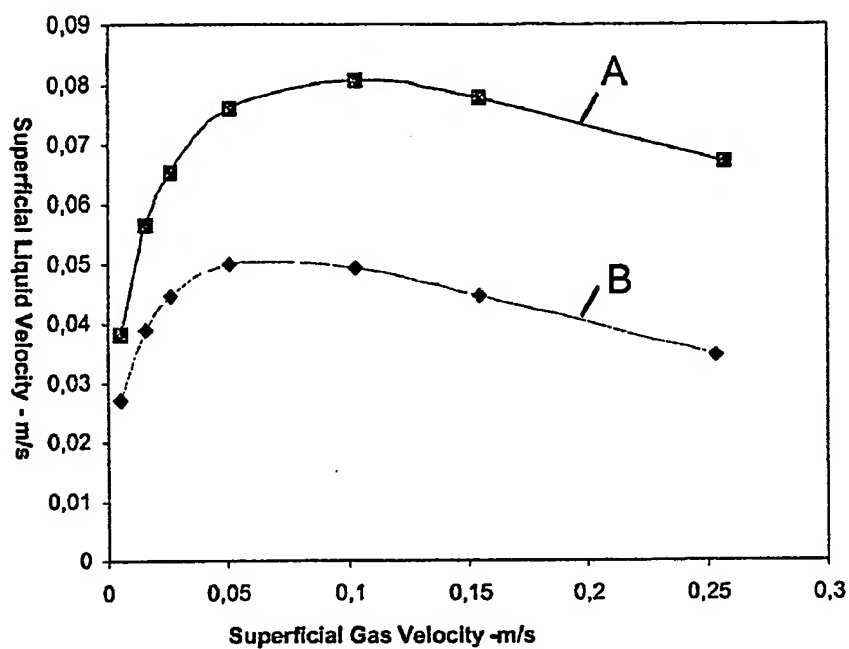


Fig. 7

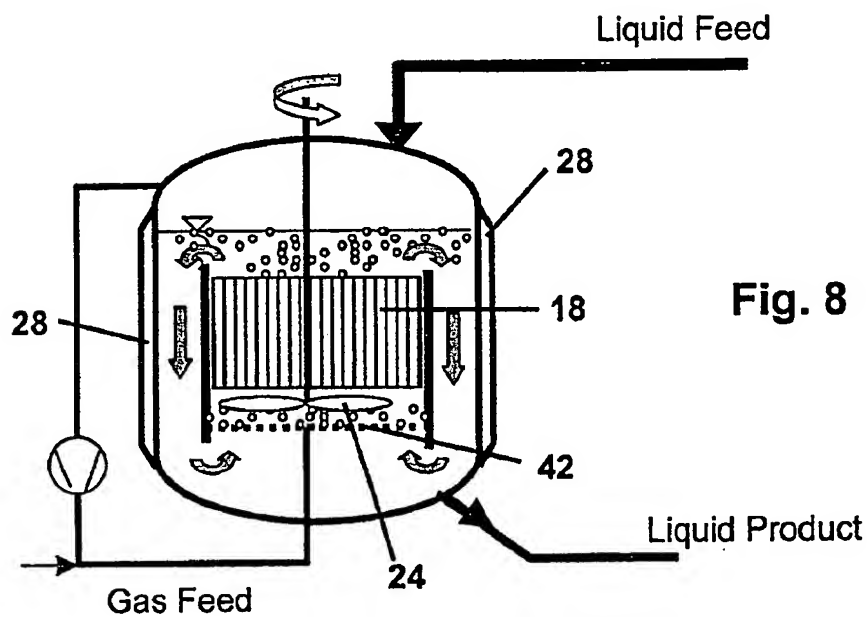


Fig. 8

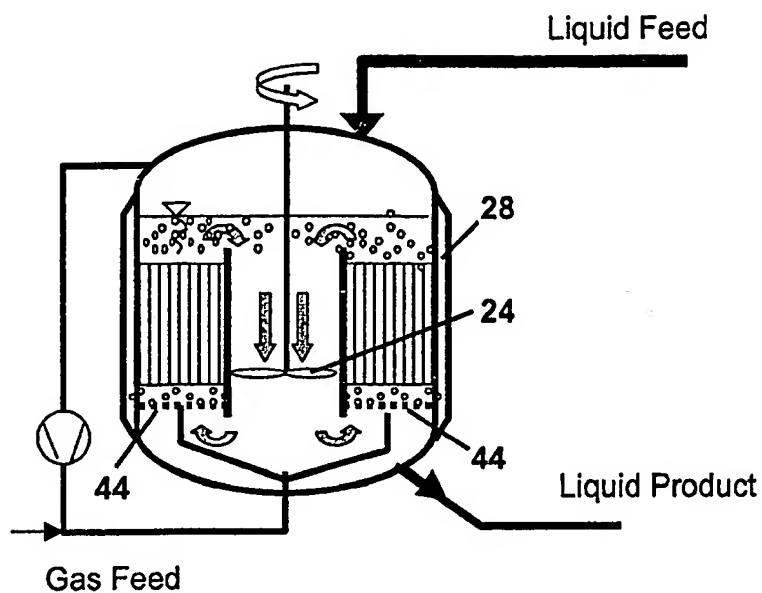


Fig. 9

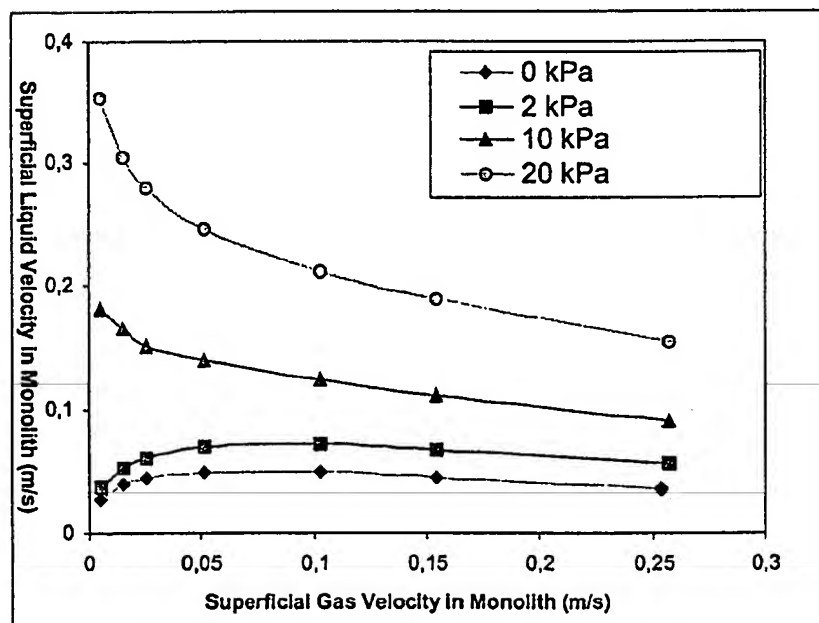


Fig. 10

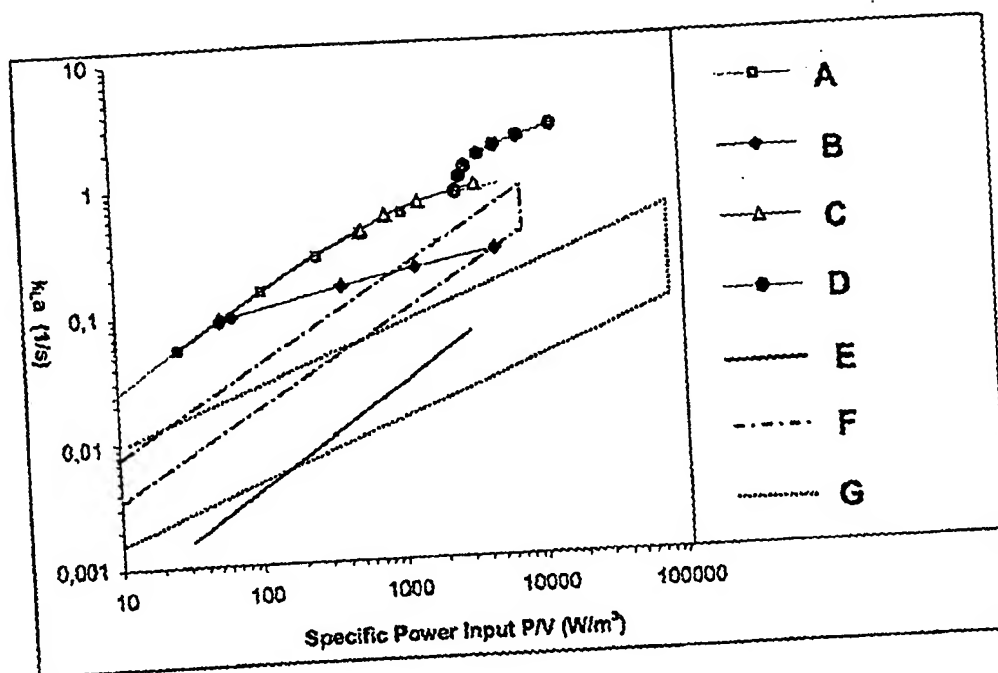


Fig. 11

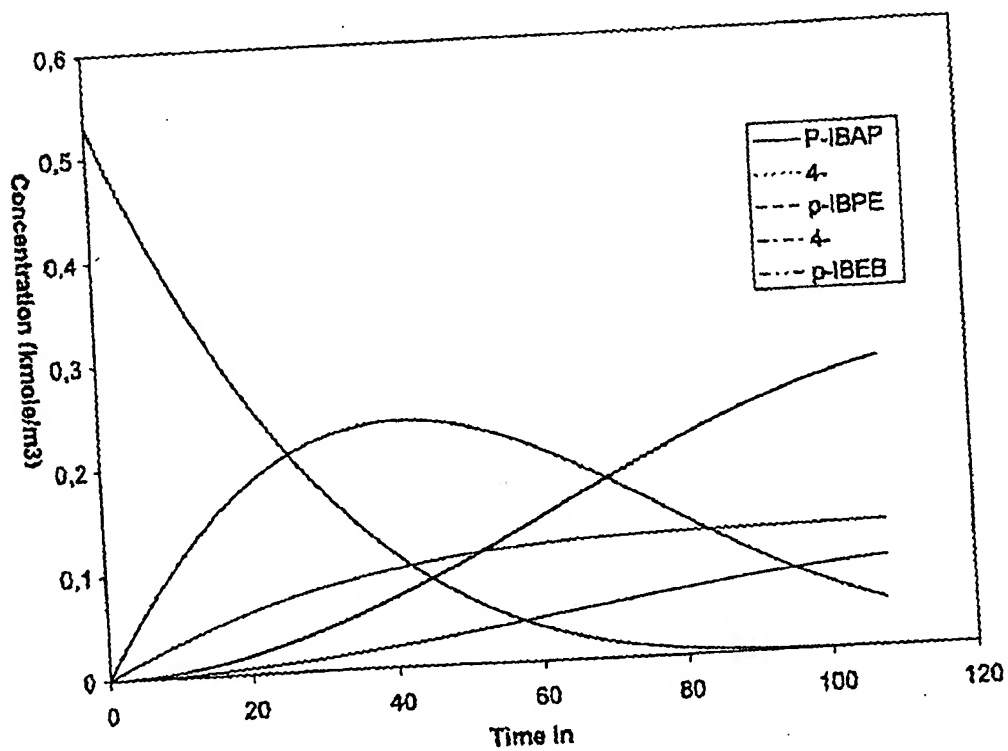


Fig. 12



## MONOLITH LOOP REACTORS

### BACKGROUND OF THE INVENTION

[0001] This invention relates to design improvements for catalytic reactors and other mass or energy transfer systems used to process liquid solutions or mixtures in the chemical industry, and particularly includes new designs for recirculating or so-called loop reactors incorporating honeycomb monoliths as essential catalyst-supporting or flow-regulating structures.

[0002] The chemical industry employs a wide variety of recirculating tank or batch reactors for chemically or physically processing chemical mixtures that include liquid solutions or mixtures, examples of specific reactor types including stirred tank, bubble column, and jet loop reactors. Many reactors of above mentioned type and of the prior art utilize solid catalyst granules or particles which are dispersed within a liquid medium comprising one or more reactants via stirrers or agitators, or via the addition of momentum through gas or liquid streams, to produce a product. When a gas is required to produce the product, it is usually fed into the reactor below the agitator, so that the agitator may also serve in the re-dispersion of large bubbles which may form in the reactor.

[0003] Although such stirred tank, bubble column, and jet loop reactors are usable for both continuous as well as for batch production, the catalytic particles experience continual attrition and must be separated from the reactant liquid to obtain the final product liquid. The required separation of the catalyst particles requires additional apparatus and operating procedures that add significant cost. Further, even with agitation, still zones with different hydrodynamic conditions exist and settling of the catalytic particles may occur.

[0004] Also, bubble size in a gas/liquid reactor is a strong function of the agitation produced. Often coalescence occurs, which produces larger bubbles, reduces gas/liquid mass transfer effectiveness, and yields unfavorable catalyst residence time distributions for the gas and sometimes the liquid.

[0005] One approach toward improving gas-liquid distribution in a tank reactor is shown in U.S. Pat. No. 4,234,650. In that patent, a gas is injected within a liquid jet into a large circulation tube within a reactor enclosure. The resulting gas/liquid mixture is then recirculated through and around the tube.

[0006] Structured or monolithic catalysts such as catalyst honeycombs offer the advantage of allowing for thin catalyst layers with high effectiveness factors and excellent mass transfer characteristics. However, as shown in U.S. Pat. No. 4,363,787, monolith use in the prior art typically involves fixed-bed, continuous-operation reactors. One variation on this approach, shown in Baltzer Science Publishers, August 1999, volume 3 (1999), page 35, circulates small moveable monoliths continuously through a reservoir of reactant liquid.

[0007] None of the prior art structured catalyst reactor designs have offered sufficient practical or economic advantages to displace any of the stirred tank, bubble column, and jet loop designs used for commercial processes. Thus the disadvantages attending the use of particulate catalysts in such reactors have not yet been overcome.

### SUMMARY OF THE INVENTION

[0008] In view of the foregoing, the present invention provides an improved method and apparatus for transforming a chemical reactant into a desired product using a fixed catalyst. In particular, the invention provides improved recirculating catalytic tank reactors for processing a liquid medium (a mixture, solution, or suspension comprising at least one liquid phase) utilizing a monolithic honeycomb catalyst bed in combination with internal agitation flow means for circulating and recirculating a liquid comprising reactants and products around and through the channels provided within the honeycombs. The reactants and products may comprise single species or mixtures, and may be present in the liquid medium as dissolved or dispersed gases, liquids, or solids.

[0009] These recirculating reactors, hereinafter termed monolith loop reactors and including reactor types such as jet loop, stirred tank and bubble column reactors, produce the improved operational results such as controlled reactor behavior, excellent kinetic properties, and a high effectiveness factor. Moreover, the improved reactors do not have the problems related to catalyst handling associated with typical slurry reactors. Specifically avoided are problems relating to separation of the catalyst particles from the product stream, settling of the catalytic particles within the reactor, and continual attrition of the particles.

[0010] The loop reactors of the present invention include at least one honeycomb monolithic catalyst, formed of catalytic material or comprising a substrate with a suitable catalyst provided on surfaces thereof, fixedly positioned within the tank. At least one bypass passageway is provided adjacent the catalytic substrate, and internal agitator means are provided to recirculate liquid medium comprising reactants through the catalyzed flow channels of the monolith and about the monolithic substrate by means of the bypass passageway. Reactor designs for both two-phase (liquid-solid catalyst) and three-phase (gas-liquid-solid catalyst) chemical, biochemical and petrochemical processes are provided. Internal agitators for the liquid medium may comprise mechanical, liquid jet, or gas bubble agitators.

[0011] The reactor designs of the invention may also be adapted for use in other fluid processing applications, examples of such applications including adsorption, absorption, or extraction processes for promoting mass or energy transfer among any two or three of a liquid phase, a gas phase, and a solid material disposed on or in the honeycomb monolith. A useful liquid processing apparatus for such applications includes a suitable liquid containment vessel in which the honeycomb monolith is disposed, the honeycomb being positioned between upper and lower collection chambers in the vessel.

[0012] For these applications the honeycomb may or may not be provided with a catalyst or adsorbent, but in any case it will incorporate a plurality of parallel open channels connecting the upper and lower chambers. Also included within the containment vessel will be at least one by-pass conduit or passageway connecting the upper and lower chambers, that passageway providing a return path for the recirculation of gases and liquids in the vessel through the honeycomb. Again, energy for driving the recirculation may be supplied by mechanical, liquid or gas bubble agitation

means such as a blade stirrer, gas sparger, liquid jet, or liquid jet/gas ejector system of the kind employed with jet loop reactors.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0013] The invention may be further understood by reference to the drawings, which are not intended to indicate scale or relative proportions of the elements shown, but wherein like reference characters designate like or corresponding parts in the various figures:

[0014] FIG. 1 is a schematic view of a tank reactor of the present invention showing a centrally positioned honeycomb monolithic catalytic substrate and a blade type of agitator flow means.

[0015] FIG. 2 is a schematic view of a tank reactor of the present invention showing a peripherally positioned honeycomb monolithic catalytic substrate with a blade type of agitator flow means.

[0016] FIG. 3 is a schematic view of a tank reactor of the present invention showing a centrally positioned honeycomb monolithic catalytic substrate and a gas header type of agitator flow means.

[0017] FIG. 4 is a schematic view of a tank reactor of the present invention showing a peripherally positioned honeycomb monolithic catalytic substrate with peripherally positioned gas header type of agitator flow means.

[0018] FIG. 5 is a schematic view of a tank reactor of the present invention showing a peripherally positioned honeycomb monolithic catalytic substrate with both blade type and gas header type agitator flow means.

[0019] FIG. 6 is a schematic view of a tank reactor of the present invention showing a peripherally positioned honeycomb monolithic catalytic substrate with centrally positioned gas header type of agitator flow means.

[0020] FIG. 7 is a graph illustrating liquid and gas flow velocities through a tank reactor.

[0021] FIG. 8 is a schematic view of a tank reactor of the present invention showing a centrally positioned honeycomb monolith catalyst with centrally positioned gas header and blade type agitator flow means.

[0022] FIG. 9 is a schematic view of a tank reactor of the present invention showing a peripherally positioned monolithic honeycomb catalyst with peripherally positioned gas header agitator flow means and a centrally located blade type agitator flow means.

[0023] FIG. 10 is a graph illustrating liquid and gas flow velocities through a tank reactor such as illustrated in FIG. 8 of the drawings.

[0024] FIG. 11 is a graph illustrating the effect of reactor power input on mass transfer efficiency for a reactor of the invention.

[0025] FIG. 12 is a graph of reactant concentration versus time for a chemical reaction carried out in accordance with the invention.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0026] Various specific reactor constructions provided in accordance with the invention are effective to overcome the

forementioned problems relating to conventional stirred tank, bubble column and jet loop reactors. Thus the specific examples of reactor designs hereinafter more particularly described are intended to be merely illustrative of the invention, rather than limiting.

[0027] Referring first to FIG. 1, a monolith loop tank reactor 10 is shown having a reactant liquid feed inlet and a liquid product outlet. The liquid level within the tank 10 is shown at 11. A cylindrical honeycomb monolithic substrate 12, retained in a tube type basket container 14, is fixedly positioned centrally of the tank diameter by suitable support rods or brackets 16. The substrate 12 has a plurality of longitudinal flow channels 18 extending therethrough, and a suitable catalyst is deposited on the surfaces of such channels. A ring-shape or annular bypass passageway 20 extends between the tubular container 14 and inner wall portions 22 of the reactor tank 10. A blade type propeller or agitator 24, mounted on a rotatable rod or shaft 26, functions as an internal flow generator for the transport of liquid through the catalyzed flow channels 18 of monolithic substrate 12 and the re-circulation of reactant liquid within bypass passageway 20, as shown by arrows a.

[0028] If desired, the tube container 14 with the substrate 12 and the rod 26 with agitator 24 may be fixed to a removable cover portion 15 of the reactor 10. The blade agitator 24 on shaft 26 is concentrically positioned for functionality within tube container 14, however it may be located above the monolith and thereby closer to the reactor cover to reduce mechanical stresses commonly applied to long stirrer shafts. A heat exchanger 28 may be utilized for heat exchange through the reactor wall. Alternatively, conventional heat exchange structures internal to the reactor or comprising an external circulation loop through a heat exchanger (not shown) may be provided.

[0029] The monolith loop reactor 30 of FIG. 2 is similar in many respects to reactor 10 of FIG. 1, except that an annular honeycomb monolithic substrate 32 is retained in a ring or annular shape container 34 fixedly positioned to inner wall portions 22 of reactor 30. A central bypass or flow passageway 36 is formed centrally of the annular substrate. Blade agitator 24 mounted on rotatable rod or shaft 26 is positioned within the passageway 36 and functions as an internal flow generator for the flow of liquid through the catalyzed flow channels 18 of monolithic substrate 32 and the re-circulation of reactant liquid within bypass passageway 36, as shown by arrows b.

[0030] The embodiments shown in FIGS. 1 and 2 easily lend themselves to simple and straight forward retrofit to existing stirred reactors. The required catalyst surface areas and hydrodynamic conditions such as velocity in the channels are easily adjusted. The reactors may be designed with any height/diameter ratio, since the liquid mixing and reactor behavior is defined only by the recirculation ratio (velocity/(2 times reactor height)). The higher the recirculation ratio, the closer the behavior is like a conventional stirred tank reactor, and the lower the recirculation ratio, the closer the behavior is like a plug flow reactor. The blade agitator not only provides for the circulating flow of the liquid within the reactor, but also serves to disperse liquid phases when more than one liquid phase is present. Also, the required mechanical energy is comparable, if not better than that required for standard stirred tank reactors, since the pressure

drop of the monolith is relatively low and the liquid/catalyst interface is improved due to the defined catalytically charged flow paths for the liquid. Accordingly energy losses due to ineffective dissipation are minimized.

[0031] The monolithic loop reactor embodiments 40 shown in FIGS. 3, 4, 5 and 6 are adapted for a three-phase or solid catalyzed gas/liquid reaction, and have a recirculating gas feed system with a control valve 38. It will be noted that the position of the honeycomb monolithic substrate 12 of FIG. 3 is similar to that of FIG. 1, whereas the position of the honeycomb monolithic substrate 32 of FIGS. 4, 5 and 6, is similar to that of FIG. 2. However, the internal flow agitator utilized in the embodiments of FIGS. 3 and 4 is in the form of a gas header or sparger. In FIG. 3, the header or sparger 42 is in the form of a disk positioned within container 14 below monolith 12, whereas in FIG. 4, the header or sparger 44 is in the form of a ring or annulus and positioned within container 34 below monolith 32.

[0032] With spargers 42 and 44 being positioned below the monoliths 12 and 32, respectively, the upward flow of gas bubbles 46 from the agitators 42, 44 through the monoliths provide the internal flow means for circulating reactant liquid upwardly through channels 18 within the monoliths and downwardly along the bypass passageways as shown by arrows c and d. The resulting difference in density between the upward-flowing gas/liquid mixture in the monoliths and the pure liquid in down-comer bypass passageways 20 and 36 functions to enhance the driving force of flow. That is, the "lighter" gas/liquid mixture tends to rise, whereas the "heavier" pure liquid tends to flow downwardly in the bypass passageway. The density difference between the gas/liquid mixture and the pure liquid together with the size of channels 18 must be considered so that frictional flow losses through the monolith are minimized.

[0033] It will be noted that the separation of the gas bubbles 46 from the liquid occurs in the top cover area 15 of the reactors 40. The gas from headers 42, 44 may be recycled and forced back, together with fresh gas, into the reactors through the gas supply system. The gas/liquid separation from the product liquid is easily accomplished at the bottom of the reactor, where no gas bubbles are present, and no additional moving parts are required. If more flow is desired through the monoliths, a blade agitator may be added in a manner similar to the embodiments of FIGS. 1 and 2.

[0034] The construction of the reactor embodiment of FIG. 5 is similar in many respects to that of FIG. 4, but with a reverse flow pattern. That is, instead of an annular agitator header 44 below the monolith for forcing flow upwardly through the channels of the monolith, a disk agitator header or sparger 42 is positioned within the central bypass passageway 36 for creating a recirculating flow within the reactor 40 as shown by arrows e. The reactant liquid in passageway 36 is saturated with gas bubbles 46 from the gas feeder system before it is fed into the catalyzed channels 18 of the monolith substrate 32. As shown, blade type agitators or stirrers 24 attached to a rotatable rod 26 may be included in passage 36 if desired to minimize bubble size and optimize gas/liquid mass transfer, as well as to support the natural direction of flow within the reactor.

[0035] The reactor embodiment shown in FIG. 6 is similar to that of FIG. 5, except that no mechanical flow agitator is utilized with the bubble flow agitator. As shown in FIG. 6,

the recirculating flow of the reactant liquid, as shown by arrows e, is the same as that shown in FIG. 5. That is, the flow generated by the gas feed from agitator header 42, producing upwardly moving bubbles 46 in passageway 36, provides sufficient internal flow means for circulating reactant liquid through catalyzed channels 18 of monolith 32 and along bypass passageway 36 adjacent the monolith.

[0036] The efficiency with which bubble flow agitation drives the recirculation of reactants through honeycomb catalyst beds depends on a number of factors including the cell density and wall thickness of the honeycombs, the density and viscosity of the gas and liquid phases, and frictional effects governing the impedance to fluid flow within the channels of the monoliths. However, the hydrodynamic operating characteristics of these reactors can be predicted with reasonable accuracy based on existing knowledge concerning frictional effects on fluid flow and the densities and viscosities of candidate liquids and gases.

[0037] FIG. 7 of the drawing is a plot showing the relationship between superficial gas velocity within the channels of a monolith and the resulting superficial liquid velocity within those channels generated from bubble gas-lift. The velocities are reported in meters/second on the horizontal and vertical graph axes, respectively.

[0038] The data plotted in the graph of FIG. 7 are for two cylindrical monolithic honeycomb catalyst beds A and B, of 200 and 400 cells/in<sup>2</sup> (31 and 62 cells/cm<sup>2</sup>, respectively) channel density, respectively, these honeycombs having channel wall thicknesses of 0.0075 inches (0.19 mm) and 0.0065 inches (0.165 mm), respectively. All walls in these honeycombs support an internal catalyst coating of 20  $\mu$ m thickness, and both monoliths have a cross-sectional area 3.14 m<sup>2</sup> and a height to diameter ratio of 1:1.

[0039] The results shown are for the case where the monoliths are disposed within a cylindrical tank reactor vessel of 4.91 m<sup>2</sup> cross-section, the difference in cross-section between each monolith and the reactor vessel making up the cross-sectional area of the down-comer spaces within the reactor. The fluid viscosities and densities used are those for a liquid phase of water and a gas phase of hydrogen at 40° C. and a pressure of 20 bar.

[0040] As FIG. 7 suggests, honeycomb channel diameter has a large effect on frictional flow resistance within the channels, reflected in the large differences in liquid velocity at equivalent gas velocities within these structures. Also evident from FIG. 7 is the fact that maximum superficial liquid velocities are attained only over a relatively narrow range of gas velocities. Higher gas velocities actually cause a decrease in liquid velocities in these structures.

[0041] The hydrodynamic liquid/gas flow behavior illustrated in FIG. 7 is typical of honeycomb monolith catalyst structures and is seen over a wide range of liquid densities, liquid viscosities, and channel sizes. At any fixed gas flow velocity within the ranges shown, higher liquid viscosities, or lower liquid densities, decrease liquid flow velocity through the channels. However, maximum liquid flow velocities are still attained only in a limited range of gas flow velocities.

[0042] Hydrodynamic performance characteristics like those of FIG. 7 are also observed over a wide range of honeycomb sizes. Flow velocities are largely independent of

catalyst bed height, since both frictional flow effects and the mass of liquid being transported through the channels at any time depend directly on channel length. Increases in bed cross-section do not change the flow velocities either, although the recirculation number (number of volumes of reactant processed through the catalyst bed per hour) increases in direct proportion to the area of the bed, provided down-comer capacity is not limiting.

[0043] All of the foregoing reactor designs offer significant advantages over packed bed, or stirred tank, bubble column or jet loop reactors for many applications. However, still further advantages in process control and reactor performance for three-phase reactions are achieved through the use of special reactor configurations that include provisions for independent gas and liquid flow control. Examples of such reactors are schematically illustrated in FIGS. 8 and 9 of the drawings.

[0044] The reactor embodiment shown in FIG. 8 is similar to that of FIG. 3, except that both a mechanical flow agitator 24 and a disk-shaped bubble flow agitator 42 are provided within the reactor vessel. The recirculating flowpath of the reactant liquid indicated by arrows f is analogous to that shown in FIG. 3. However, in the case of the FIG. 8 reactor, liquid flow is controlled not only by the gas feed from agitator header 42, producing upwardly moving bubbles in honeycomb channels 18, but also by mechanical agitator 24. Thus agitator 24 can add to or reduce the flow of liquid into channels 18 resulting from gas bubble lift alone.

[0045] The reactor embodiment shown in FIG. 9 is similar to that of FIG. 4, except that again both a mechanical flow agitator 24 and an annular bubble flow agitator 44 are provided. The recirculating flowpaths of the reactant liquid indicated by arrows g is the same as that shown in FIG. 4, but with liquid flow velocity in this case being a product of both the gas feed from agitator header 44 and mechanical agitator 24. Again, mechanical agitator 24 can add to or reduce the flow of liquid into channels 18 at most available gas flow rates.

[0046] Of course, in either of the embodiments of FIGS. 8 and 9 the blade-type mechanical agitator is only representative of the various means by which liquid flow through the channels of the honeycomb catalyst may be independently controlled. Other flow control means such as liquid jets, including jets arranged to handle externally recycled volumes of the processed reactants, may additionally or alternatively be employed.

[0047] The added ranges of gas and liquid flow achievable in these reactor designs is illustrated in FIG. 10 of the drawings. That illustration is a graph plotting liquid flow velocity against gas flow velocity for four different operating conditions of a reactor having a design such as shown in FIG. 8 of the drawings. The operating conditions reported are developed through the application of additional mechanically generated liquid circulation driving forces. Those additional forces create additional liquid pressure drop across a honeycomb monolith at selected values from zero to 20 kPa, the higher pressure drops being generated by mechanical agitator operation at higher stirring speeds.

[0048] The honeycomb monolith in the reactor characterized in FIG. 10 has a cell density of 400 cell/in<sup>2</sup> (62 cells/cm<sup>2</sup>) and a honeycomb cross-section of 3.14 m<sup>2</sup>, with

a wall and coating thickness similar to the honeycomb of the same geometry described above with reference to FIG. 7. The characterization presented is for a liquid phase of water and a gas phase of hydrogen at 40° C. and a 20 bar pressure.

[0049] Evident from a study of FIG. 10 are the wider ranges of liquid and gas linear velocity observed within the reactor, these being the result of the new degree of freedom available through the application of the additional mechanical liquid driving force. This added force permits reactor operation over a much wider range of variation in the ratio of gas to liquid flow in the monolith. For example, high liquid flow velocities can be achieved at zero or low gas flow velocities, an operating mode that substantially increases the recirculation number for the reactor. This brings conditions within the reactor closer to those of an ideally mixed system. Another significant advantage of the higher recirculation number is an increase in the heat exchange efficiency of the reactor, where such is useful for process control.

[0050] A general measure of the efficiency of any system for contact or mass transfer among two or more phases within a vessel is the achieved mass transfer coefficient,  $k_L a$ , as a function of the energy input per unit volume of fluid in the vessel. This value is useful for the evaluation of apparatus for carrying out physical processes such as absorption, separation or heat exchange as well as for catalytic chemical reactors involving mass transfer among gas, liquid and/or solid phases. Higher  $k_L a$  values can be achieved either through a higher gas/liquid/solid contact area (a larger honeycomb) or higher energy input to the reactor. Thus if the energy input per unit volume of liquid in a given monolithic honeycomb reactor is fixed at a predetermined value, then the value of  $k_L a$  will increase with honeycomb volume due to the larger catalyst wall area presented by additional channels or longer channel walls.

[0051] Gas-liquid mass transfer occurring within reactor spaces outside of the volume occupied by the honeycomb catalyst in these reactors is negligible in many reactor designs, due to factors such as the gas and liquid coalescence that quickly occurs as these fluids exit the honeycomb channels. Nevertheless, for the purpose of comparing the mass transfer efficiency of these reactors with alternative reactor designs, the measured or calculated mass transfer rates (expressed as mass transfer coefficients  $k_L a$ ) are based on the total liquid volume within the reactor vessel, rather than on liquid volume within the active catalyst alone.

[0052] For reactors of 10-15 m<sup>3</sup> liquid handling capacity that are similar in design to the reactors shown in the drawings, specific reactor power inputs of up to about 2000 W/m<sup>3</sup> can be generated gas bubble flow agitation alone. Accordingly values of  $k_L a$  in the range of about 0.1-1.2 second<sup>-1</sup> can be reached, even where the honeycomb catalyst volume is only 25-50% of the liquid phase volume. Still higher efficiencies, and/or equivalent efficiencies at significantly lower energy inputs, can be achieved using a combination of gas and mechanical agitation for input power.

[0053] FIG. 11 of the drawing is a graph plotting mass transfer coefficient  $k_L a$  against reactor input power in watts/m<sup>3</sup> for a number of different reactor operating conditions. The data presented in the graph are for a reactor of 4.91 m<sup>2</sup> cross-section and 2.5 m height, the catalyst consisting of a honeycomb having 62 vertically-oriented channels per cm<sup>2</sup> of honeycomb cross section, with a cross-sectional area of

3.14 m<sup>2</sup> and a height of 1.5 m. The liquid phase within the reactor is water, and the gas phase is air at 1 bar pressure and 20° C.

[0054] Included in FIG. 11 are data for bubble flow operation alone, covering a range of power inputs resulting from different gas flow rates, as well as data for three different cases involving energy input from a combination of bubble flow and stirring. In the latter three cases, gas flow is fixed at a predetermined level and higher input energies are reached by stirring at increasing rates to increase the liquid recirculation through the catalyst. FIG. 11 also plots  $k_L a$  values as a function of input energy for three competing batch reactor types. The data presented for the competing designs are considered to be representative of the performance of stirred tank, bubble column, and jet loop reactor designs.

[0055] Referring more particularly to FIG. 11, Curve A plots  $k_L a$  as a function of reactor input power for the case of bubble flow agitation only. Curves B, C and D plot  $k_L a$  values for combinations of bubble agitation with propeller blade stirring. The latter curves are plotted for three different fixed gas feed rates.

[0056] Curve A covers a range of gas feed rates from zero to about 5000 m<sup>3</sup>/hour (at standard temperature and pressure). Curves B, C and D show the energy and reactor efficiency increases from added mechanical stirring, starting at the base energy levels corresponding to the gas-only agitation points of 100 m<sup>3</sup>/hr, 1000 m<sup>3</sup>/hr, and 5000 m<sup>3</sup>/hr on curve A. Thus the increases in input power and transfer efficiency above the gas-only values falling on curve A (i.e. the values at the junctions of curves B, C and D with curve A) all result from increases in the stirring rate alone.

[0057] As is evident from a study of FIG. 11, the increase in  $k_L a$  and mass transfer with mechanical agitation reflected at the lowest gas flow rate (100 m<sup>3</sup>/hr-Curve B of the drawing) is smaller than could be achieved using equivalent power input from bubble agitation. However, that increase is still significant for reactions that need to be carried out at high liquid flow velocities.

[0058] At the fixed gas feed rate of 1000 m<sup>3</sup>/hr plotted on Curve C, the power input through the mechanical agitator yields the same increase in mass transfer as if more gas was added. Thus over the overlapping ranges of reactor input power level, the gas:liquid ratio within the catalyst bed may be arbitrarily adjusted to best meet the requirements of any selected chemical process. Curve D indicates that, at gas feed rates above 1000 m<sup>3</sup>/hr, additional mechanical agitation increases the mass transfer coefficient of the reactor to values well above those achievable through bubble agitation alone.

[0059] Curves E, F, and G in FIG. 11 compare the monolith loop reactor of Curves A-D with various conventional gas-liquid mass transfer systems. The data for these latter systems are based on literature measurements for oxygen transfer into an aqueous liquid phase, the latter phase in some cases containing some additives to suppress gas and liquid coalescence for improved mass transfer performance. The values covered in FIG. 11 for a stirred tank reactor design (Curve F) and a jet loop reactor (Curve G) reflect upper and lower limits for a range of mass transfer efficiencies at each energy level, base on performance ranges from the literature. In the case of the bubble column reactor, only one data set is plotted.

[0060] The higher efficiency and improved mass transfer performance of the monolith loop reactors over the competitive designs characterized in FIG. 11 are evident. Thus, over most of the useful range of input power, monolith loop reactors provide significantly higher mass transfer rates at lower energy inputs than any of the other designs provide. And, these advantages are secured even in operating modes where the power input to the monolith reactor is provided by bubble agitation alone, the latter modes being particularly advantageous since no mechanical systems for the input of stirring or other mechanical agitation are required.

[0061] A specific example of a commercial process wherein a monolith loop reactor would provide significant processing advantages is the selective hydrogenation of p-isobutyl acetophenone (p-IBAP) to the ibuprofen intermediate p-isobutyl phenyl 2-ethanol (p-IBPE). This reaction is conventionally carried out in a methanol solvent in stirred tank reactors containing particulate ruthenium/alumina catalysts. Side reactions such as (i) the hydrogenation of the aromatic ring of p-IBAP to produce 4isobutylcyclohexyl methyl ketone, (ii) the hydrogenation of p-IBPE to produce 4isobutylcyclohexyl-2-ethanol, and (iii) the hydrogenation of the OH-group of p-IBPE to produce p-isobutyl ethylbenzene are commonly observed, and alternative palladium/carbon and Raney nickel catalysts have been suggested to control such reactions.

[0062] FIG. 12 of the drawing shows transient reactant and product concentrations for this process calculated for the case of a honeycomb loop reactor incorporating a monolithic honeycomb catalyst having a cell density of 400cps (62 cells/cm<sup>2</sup>), the channels being coated with a 5  $\mu$ m thick layer of a Ru/Al<sub>2</sub>O<sub>3</sub> catalyst and reactor operation being at a pressure of 47.6 bar and a temperature of 386° K. The transients shown in FIG. 12 are quite similar to those reported in the literature for slurry reactors employing particulate ruthenium/alumina catalysts, but significant processing and cost advantages can be secured if monolith loop reactors are used instead.

[0063] Among the advantages of the monolith loop reactor design are a somewhat lower specific power input requirement, since providing the hydrogen reactant through the reactor bubbler system increases channel flow and reactor mass transfer at no added cost. Further, filtering to separate the catalyst from the reactant mixture is not required, avoiding the need for filtration equipment and the inevitable loss of catalyst in the course of filtration. And, catalyst effectiveness can be further increased simply by increasing the catalyst loading on the monolith, whereas higher catalyst loadings in slurry systems increase catalyst attrition as well as reactor stirring power requirements.

[0064] Another characteristic advantage of monolith loop reactors such as herein described is an added safety margin for the control of "run-away" exothermic reactions. Self-accelerating reactions wherein reaction rate increases exponentially with temperature can cause reactor heating beyond the point where the available means for heat removal are adequate to deal with the exotherm. In most slurry reactors these run-away processes can only be controlled by means such as dumping with rapid catalyst separation, or by the addition of chemical "moderators" to the batch. Moderator additions are generally undesirable since they can result in batch contamination and loss of the entire batch.

[0065] In the monolith loop reactors of the invention, these difficulties are conveniently overcome simply by providing mechanical means for dumping reactants from the tank or rapidly withdrawing the monolithic catalyst from the reaction mixture. In either case the reactants rapidly drain and separate from the monolithic catalyst, quickly terminating the reaction without damage to the reactants or products present in the mixture.

[0066] As will be apparent from the foregoing description, the invention is not restricted to the particular examples of reactor designs or processes hereinabove described, which are intended to be illustrative rather than limiting. For example, gas-liquid contacting or reaction systems can readily be provided wherein mechanical agitation is used to force gas and liquid downflow through the honeycomb catalyst, rather than upflow through the catalyst as in FIGS. 8 and 9 of the drawings. Designs of this type can provide longer gas-liquid contact time since, after passage through the catalyst, the gas remains dispersed in the liquid phase as it traverses the up-comer conduits within the reactor.

[0067] This extra contact time can be particularly significant in reactors configured to contain honeycomb catalysts of high length:diameter ratio. However, even in upflow reactors, the use of high length:diameter honeycombs offers a contact time advantage since bubble coalescence is suppressed for so long as the gas bubbles remain confined to the channels of the honeycomb. And, bubble rise times fall in a relatively narrow range since the bubbles are typically all of similar size.

[0068] It is also possible, in the case of downflow reactors, to deploy supplemental honeycomb catalysts in the up-comer space within the reactor. For reactors operating in this mode the driver for fluid circulation up the honeycomb channels can be bubble agitation alone.

[0069] Of course, as previously noted, the reactor designs disclosed herein may also be adapted for use in mass or energy transfer applications wherein liquid or liquid-gas mixtures are processed for purposes other than carrying out chemical reactions therein. Thus the fluid channeling characteristics of honeycomb monoliths can offer significant advantages for any recirculation-based chemical or physical adsorption, absorption, stripping or mixing process wherein mass or energy exchanges among two or more gas, liquid or solid phases must be efficiently supported.

I claim:

1. Liquid processing apparatus comprising:

a liquid containment vessel;

a honeycomb monolith disposed within the vessel, the honeycomb being positioned between a vessel upper collection chamber and a vessel lower collection chamber, the honeycomb incorporating a plurality of open, parallel honeycomb channels connecting the upper and lower chambers;

at least one bypass passageway within the containment vessel connecting the upper and lower chambers for the recirculation of a liquid medium within the vessel; and

mechanical, liquid, or gas bubble agitation means disposed within the vessel for recirculating the liquid medium through the parallel honeycomb channels and bypass passageway.

2. Apparatus in accordance with claim 1 wherein the honeycomb monolith contains or supports a catalyst.

3. Apparatus in accordance with claim 1 wherein the vessel is provided with bubble agitation means.

4. Apparatus in accordance with claim 1 wherein the vessel is provided with both bubble and mechanical agitation means.

5. Apparatus in accordance with claim 1 wherein the by-pass conduit has a crosssectional area in the range of 10-95% on vessel cross-sections traversing the bypass passageway and the honeycomb.

6. Apparatus in accordance with claim 1 wherein the vessel has a height:diameter ratio of 0.3-100

7. Apparatus in accordance with claim 1 wherein the vessel includes internal or external loop means for transferring heat into or away from the liquid medium disposed in the vessel.

8. A chemical reactor for catalytically processing a reactant to produce a product which comprises:

a tank reactor,

a monolithic honeycomb substrate fixedly positioned within said tank,

catalytic material on wall portions of said honeycomb substrate,

at least one bypass passageway adjacent said honeycomb substrate within the tank, and

means within said tank for circulating said reactant as or within a liquid medium along the catalyzed wall portions of said honeycomb substrate and through said bypass passageway adjacent said honeycomb substrate to produce a product.

9. A reactor in accordance with claim 8 including means for feeding a reactant into said tank, and means for removing a product liquid from said tank.

10. A reactor in accordance with claim 8 wherein said monolithic honeycomb substrate has a plurality of channels extending therethrough, and said catalytic material is provided on the wall portions of said channels.

11. A reactor in accordance with claim 8 wherein said monolithic honeycomb substrate is in the form of a cylinder fixedly positioned centrally of wall portions of said tank reactor.

12. A reactor in accordance with claim 8 wherein said bypass passageway is an annular by-pass passageway extending between inner wall portions of said tank reactor and said cylindrical substrate.

13. A reactor in accordance with claim 12 wherein said internal circulating means is in the form of a blade type agitator positioned in axial alignment with said cylindrical substrate for circulating the reactant liquid through said catalyzed honeycomb substrate and through said annular bypass passageway extending between wall portions of said tank reactor and said substrate.

14. A reactor in accordance with claim 12 wherein said internal circulating means is in the form of a gas feed header type agitator positioned in axial alignment below said cylindrical substrate for forming upwardly flowing bubbles in the reactant liquid and circulating the liquid through said catalyzed honeycomb substrate and through said adjacent annular bypass passageway extending between wall portions of said tank reactor and said substrate.



15. A reactor in accordance with claim 14 including means for recirculating and regulating the flow of gas feed to said gas header agitator.

16. A reactor in accordance with claim 8 wherein said monolithic honeycomb substrate is in an annular form fixedly positioned adjacent inner wall portions of said tank.

17. A reactor in accordance with claim 16 wherein said bypass passageway is formed centrally of said annular substrate.

18. A reactor in accordance with claim 17 wherein said internal circulating means is in the form of a blade type agitator positioned within said bypass passageway for circulating reactant liquid through said bypass passageway adjacent said substrate and through said catalyzed annular honeycomb substrate.

19. A reactor in accordance with claim 17 wherein said internal circulating means is in the form of a gas feed header type agitator positioned adjacent a lower portion of said central bypass passageway for forming upwardly flowing bubbles in reactant liquid within said passageway and circulating such liquid through said central passageway and through the adjacent catalyzed annular honeycomb substrate.

20. A reactor in accordance with claim 17 wherein said internal circulating means includes both a blade agitator and a gas header agitator positioned within said central passageway for circulating reactant liquid through both said central bypass passageway and the adjacent catalyzed annular honeycomb substrate.

21. A reactor in accordance with claim 17 wherein said internal circulating means is in the form of an annular gas feed header type agitator positioned below said annular honeycomb substrate for forming upwardly flowing bubbles in reactant liquid within the honeycomb and circulating said liquid upwardly through said catalyzed annular honeycomb substrate and downwardly through said bypass passageway centrally of said annular substrate.

22. A method of producing a product from a reactant within a recirculating tank reactor which comprises,

feeding a reactant into a tank reactor,

fixedly positioning a monolithic honeycomb substrate having catalytic surfaces within said tank so as to leave room therein for at least one adjacent bypass passageway,

internally activating a flow of said reactant within said tank,

circulating such activated flow of reactant through said fixedly positioned catalyzed honeycomb substrate and through said adjacent bypass passageway, and

removing a product from said tank reactor.

23. A method in accordance with claim 22 including the step of internally mechanically activating the flow within the bypass passageway.

24. A method in accordance with claim 22 wherein the reactant is provided in a liquid medium, and wherein the step of internally activating the flow of reactant comprises forcing gas into designated portions of the liquid medium and forming upwardly flowing bubbles in such portions.

25. A method in accordance with claim 22 including the step of fixedly positioning the monolithic honeycomb substrate adjacent inner sidewall portions of the tank, and forming the adjacent bypass passage centrally of the honeycomb substrate.

26. A method in accordance with claim 22 including the step of fixedly positioning the monolithic honeycomb substrate centrally within the tank, and forming the adjacent bypass passageway between the centrally positioned honeycomb substrate and inner wall portions of the tank reactor.

27. A stirred tank reactor comprising:

a reactor enclosure having an inlet for the introduction of a reactant into the enclosure and an outlet for the extraction of a product therefrom;

a honeycomb catalyst bed mounted within the enclosure, the bed comprising a plurality of channels extending therethrough;

at least one bypass passageway within the enclosure disposed to permit the passage of the reactant and product around and past the honeycomb bed; and

recirculation means comprising a mechanical stirrer positioned within the enclosure for developing a recirculation flow within a liquid medium comprising the reactant present in the reactor, and for carrying at least a portion of the reactant along a closed flow path that sequentially traverses both the honeycomb channels and the bypass passageway.

28. A bubble column reactor comprising:

a reactor enclosure having an inlet for the introduction of a reactant into the enclosure and an outlet for the extraction of a product therefrom;

a honeycomb catalyst bed mounted within the enclosure, the bed comprising a plurality of channels extending therethrough;

at least one bypass passageway within the enclosure disposed to permit the passage of the reactant and product around and past the honeycomb bed; and

recirculation means comprising a gas bubble source positioned within the enclosure for developing a recirculation flow within a liquid medium comprising the reactant present in the reactor, and for carrying at least a portion of the reactant along a closed flow path that sequentially traverses both the honeycomb channels and the bypass passageway.

\* \* \* \* \*



US006086832A

**United States Patent** [19]  
**Ohta**

[11] **Patent Number:** **6,086,832**  
 [45] **Date of Patent:** **Jul. 11, 2000**

[54] **APPARATUS FOR EVALUATING A SOLID CATALYST AND EVALUATION METHOD USING THE APPARATUS**

[75] **Inventor:** Nobuyuki Ohta, Sodegaura, Japan

[73] **Assignee:** Idemitsu Kosan Co., Ltd., Tokyo, Japan

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[30] **Foreign Application Priority Data**

Dec. 6, 1996 [JP] Japan ..... 8-327339

[51] **Int. Cl.<sup>7</sup>** ..... B01J 8/02

[52] **U.S. Cl.** ..... 422/211; 422/106; 422/222; 422/224; 422/225; 422/242; 436/37

[58] **Field of Search** ..... 422/106, 226, 422/211, 108, 110, 187, 188, 189, 190, 193, 205, 222, 224, 225, 228, 231, 242, 68.1; 436/37

[56] **References Cited**

**U.S. PATENT DOCUMENTS**

4,937,051 6/1990 Graven et al. .... 422/194

5,133,941 7/1992 Hays et al. .... 422/140

*Primary Examiner*—Marian C. Knode

*Assistant Examiner*—Frederick Varcoe

*Attorney, Agent, or Firm*—Oblon, Spivak, McClelland, Maier & Neustadt, P.C.

[57] **ABSTRACT**

An apparatus for evaluating a solid catalyst which can enlarge a range of an applied fluid used for an evaluation of a performance of the solid catalyst and can accurately evaluate the performance of the solid catalyst on a laboratory scale and a method of evaluating a solid catalyst using the apparatus are provided. There are disclosed an apparatus of evaluating a solid catalyst, wherein a raw material feeding portion has a function capable of continuously feeding a liquid raw material or a mixed raw material consisting of a gas and a liquid, wherein a reactor in a reacting portion has an inlet for a fluid raw material and reaction product outlets for discharging a reaction product while separating it into a liquid product and a gaseous product, and wherein a recovering portion has reaction product inlets connected to each of the reaction product outlets of the reactor and has a liquid level control portion for keeping a liquid level within the reactor constant, and a method of evaluating a solid catalyst using the apparatus.

**11 Claims, 4 Drawing Sheets**

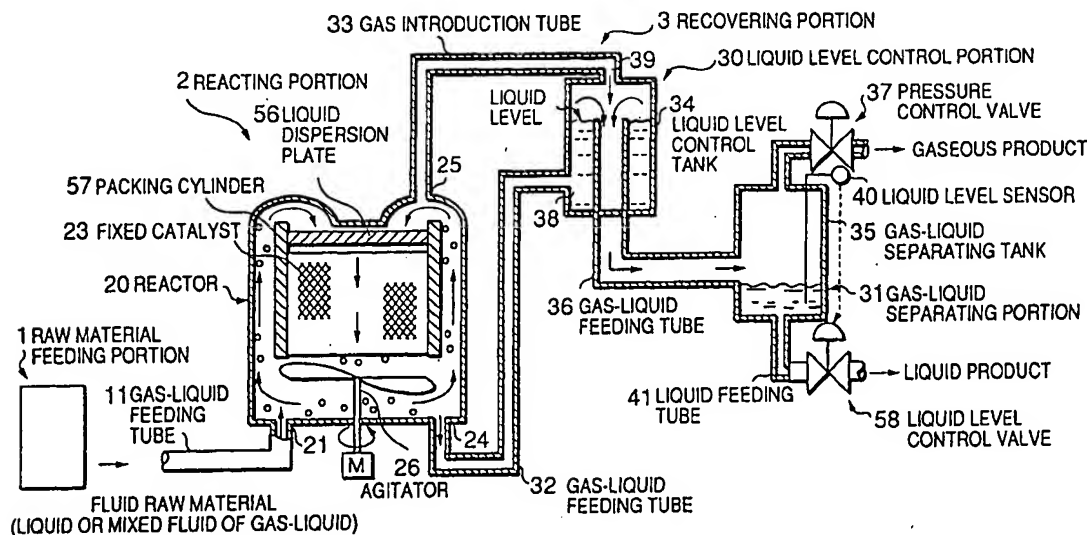




Fig. 1

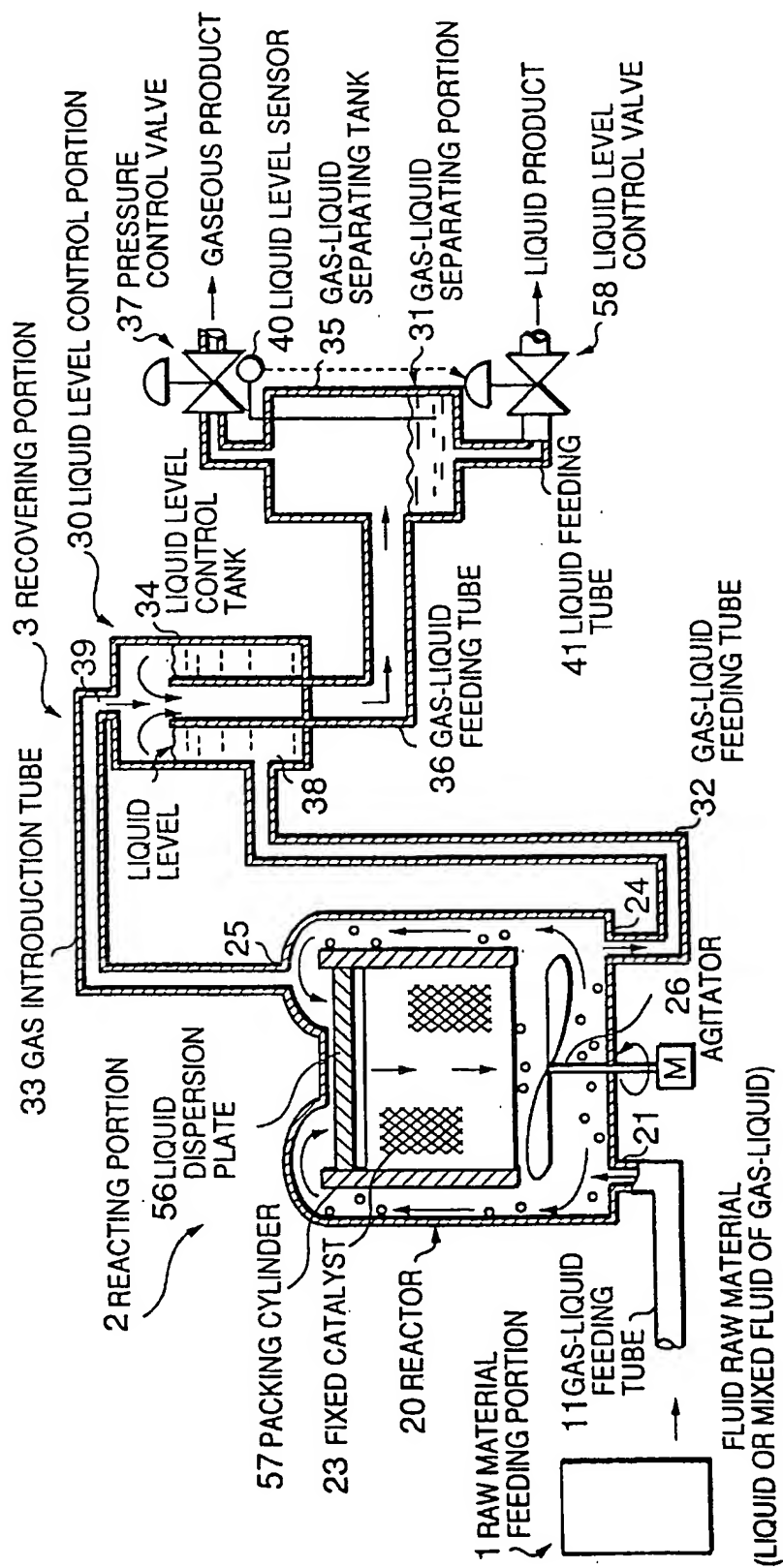


Fig.2

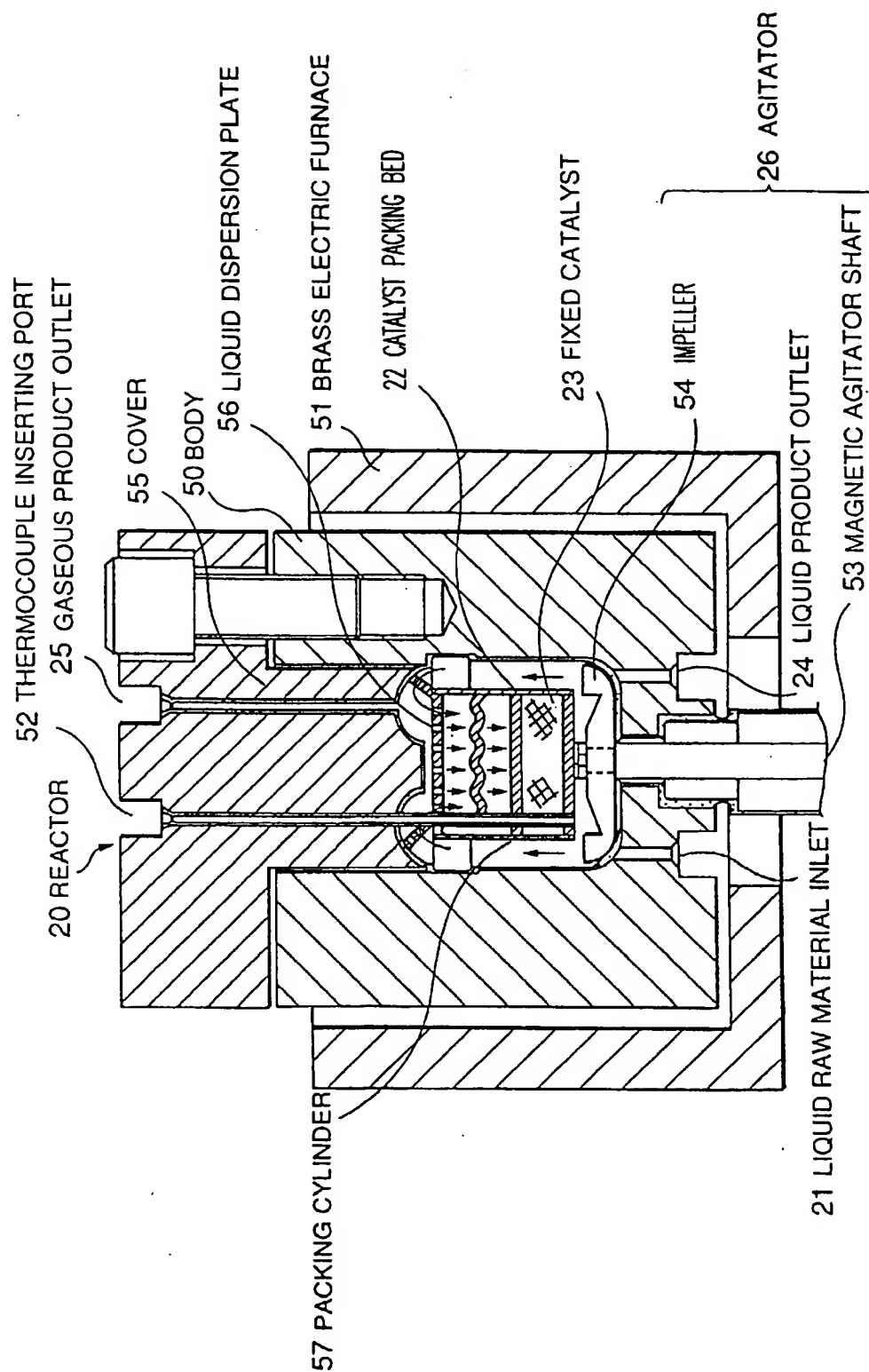


Fig.3

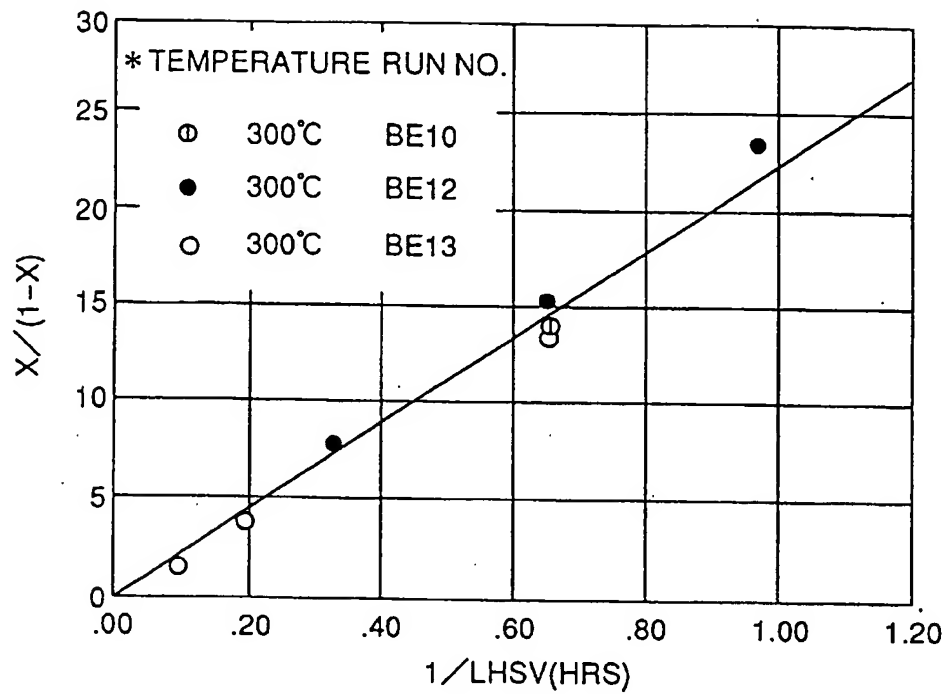


Fig.4

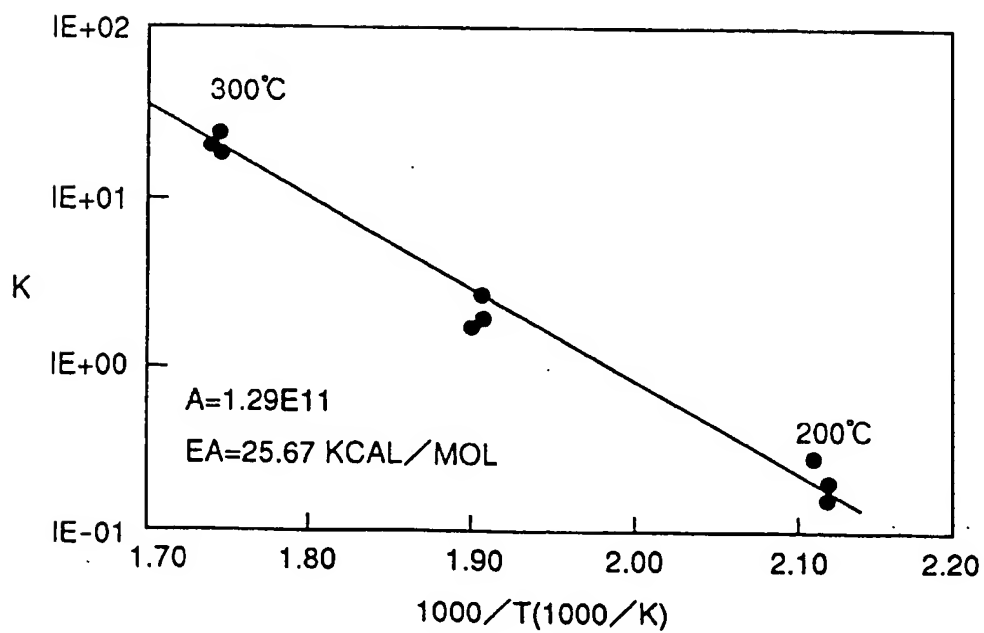


Fig.5

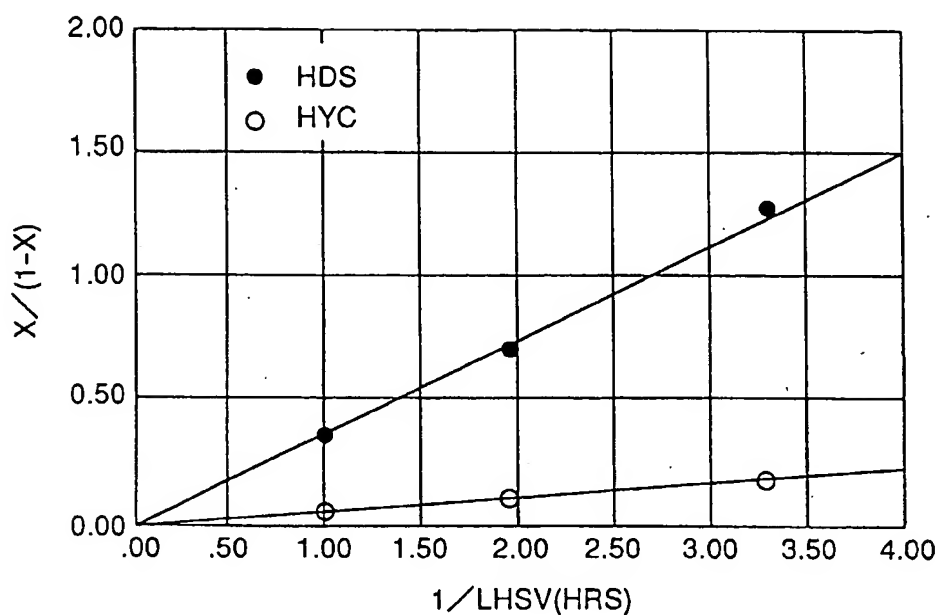
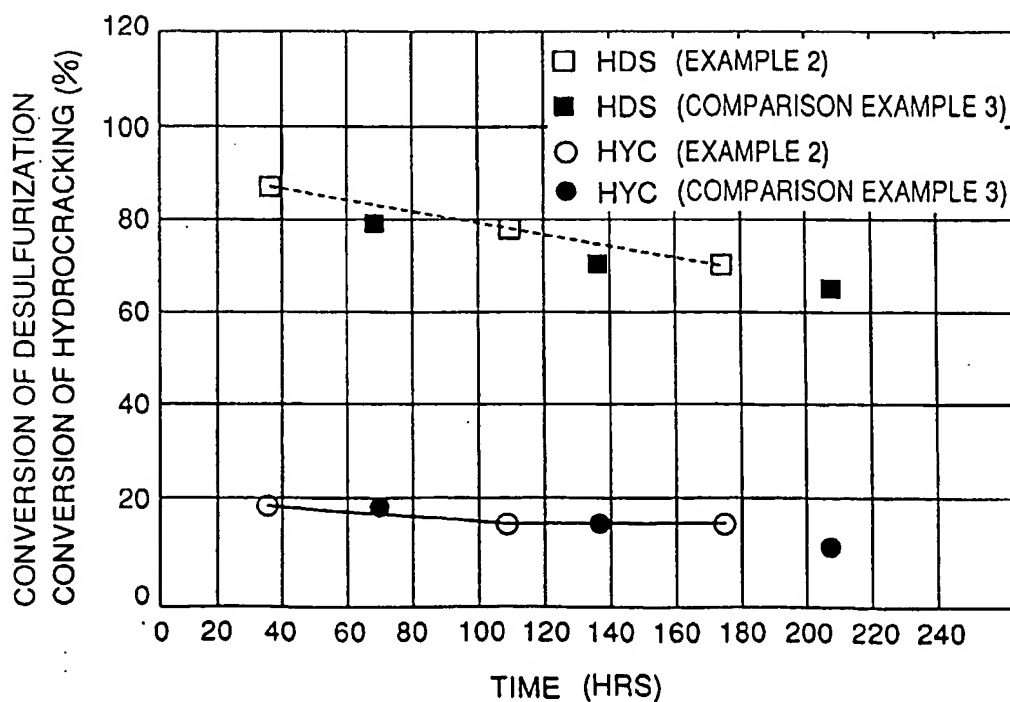


Fig.6



# APPARATUS FOR EVALUATING A SOLID CATALYST AND EVALUATION METHOD USING THE APPARATUS

## FIELD OF THE PRESENT INVENTION

The present invention relates to an apparatus for evaluating a solid catalyst and a method of evaluating a solid catalyst. More particularly, the present invention relates to an apparatus for evaluating a solid catalyst and a method of evaluating a solid catalyst using the apparatus, which are suitably used in a type of industry where a product is manufactured by a reaction apparatus using the solid catalyst, for example, an oil refining industry, a petrochemical industry, the whole field of organic and inorganic chemical industry, and a testing, research, development and quality control field with respect to a catalyst in a design, construction industry and a manufacturing industry for a solid catalyst.

## BACKGROUND OF THE PRESENT INVENTION

Conventionally, as an apparatus for evaluating an activity and life of a solid catalyst, a selectivity of a product and a quality of a product on a laboratory scale, an apparatus using an isothermal tubular reactor is frequently used.

As disadvantages of this tubular reactor, the following points have been indicated.

(1) Since a flow rate is lower than that of a large scale tubular reactor (hereinafter, referred to as an actual apparatus) used for an commercial purpose, the apparatus is effected by a mass transport limitation, so that there is a fear that the obtained evaluation results are different from that of the actual apparatus.

(2) When a diameter of the tube is too small, the apparatus is significantly effected by a maldistribution due to the wall, and when a length of a packing layer is too short, the apparatus is significantly effected by a back mixing.

(3) In a system of great endothermic reaction or great exothermic reaction, not only it is hard to maintain an isothermal condition, but also a difference is generated between a surface temperature of the catalyst (an actual reaction temperature) and a temperature of a fluid, so that it is hard to recognize the actual reaction temperature.

(4) Since the structure is made such that the fluid is successively reacted from an inlet to an outlet of the catalyst layer, a concentration of a material to be reacted, a reaction rate and a concentration of a poisoning material collected on the catalyst are largely different when seen in a finely divided section. Accordingly, it is hard to accurately obtain a reaction rate and a deterioration characteristic of the catalyst.

Therefore, hitherto, it has been a common sense that as well as the scale of the experimental apparatus has been gradually enlarged, the research and development has been proceeded while recognizing the influences of the above items (1) to (4).

Further, there has been suggested various kinds of evaluation apparatuses using a reactor each of which is designed for the purpose of solving the disadvantages of the above items (1) to (4) on a laboratory scale. The apparatus will be described below while indicating the source thereof.

### (1) Berty Reactor

1) Berty, J. M. et al.; 64th National Meeting A. I. Ch. E Preprint 42E (1969)

There are shown evaluation results (hydrogenation of ethylene) in the case that a fluid in a 5 inch type reactor

(named at the later time) is a gas phase and a chart for calculating a flow rate of a gas passing through a catalyst layer.

A summary of applied examples published later is shown in Table 1 together with cited references.

TABLE 1

Reaction used	Purpose of research	Condition of reaction	References
Hydrogenation of ethylene	Recognition of performance of reactors	100° C. 10-20 atm	2), 4)
Synthesis of methanol	Consideration of runaway condition	232° C. 52 atm	5)
Synthesis of methanol	Consideration of catalyst species and catalysis	255° C. 16 atm	8)
Dehydrogenation of cyclohexanol	Consideration of reaction kinematics	270-380° C. 1-2 atm	6)
Aromatization of n-heptane	Recognition of deteriorating behavior	370-590° C.	7)
CO oxidation	Consideration of kinematic model	160-200° C.	9)
Methanation of CO	Verification of optimum control model	237-337° C. 69 atm	10)
Sublimation of naphthalene	Consideration of deteriorating rate equation	23° C.	11)
Oxidation of SO <sub>2</sub>	Recognition of performance of reactor	0.87 atm	12)
	Consideration of kinematic equation	363-363° C. 2.5-10 atm	

### References

- 2) Berty J. M. et al., AIChE 64th National Meeting 42E (1969)
- 4) Berty J. M., Chem. Eng. Prog., 70(5), 78 (1974)
- 5) Berty J. M. et al., AIChE J., 28(6), 914 (1982)
- 6) Gut G. et al., Chem. Eng. Sci., 37(2), 319 (1982)
- 7) Mahoney J. A., J. Catal., 32, 247 (1974)
- 8) Kelly K. P. et al., J. Catal., 101, 396 (1986)
- 9) Broucek R. et al., Chem. Eng. Sci., 41(11), 2901 (1986)
- 10) Bowman R. M. et al., Appl. Catalysis, 7, 179 (1983)
- 11) Caldwell L., Appl. Catalysis, 8, 199 (1983)
- 12) Doering F. J., Chem. Eng. Sci., 43(2) 221 (1988)

2) "Continuous Operation Of The Berty Reactor For The Solvent Methanol process" Berty J. M., Tnd. Eng. Chem. Res. 30,1413-1418 (1991)

A method of successively evaluating a catalyst by introducing a synthesis gas under a state of fully filling the Berty reactor with a solvent is disclosed.

### (2) Spinning Basket Reactor

1) Myers, E. C. et al.; A. C. S. Sympo. No. 65 37 (1978)

A desulfuration reaction rate of dibenzothiophene contained in white oil is measured by using a Multi Phase spinning Basket Reactor (a name in the reference). Further, a method of performing an experiment is explained relatively in detail.

2) Ammus, J. M. et al; I. E. C. Res. 26, 494-501 (1987)

A desulfuration reaction rate of atomospheric residual oil is measured by using a spinning Basket Reactor (a name in the reference). Further, a method of performing an experiment is explained relatively in detail.

Since a liquid surface within a spinning basket reactor is not largely changed, it is considered that a successive evaluation experiment on a catalyst of three phases of gas, liquid and solid by means of the reactor can be easily performed.

(3) Other Internal Recycle Reactors of Fixed Catalyst Type  
1) Jankowski, H. et al.; Chem. Techn. (Berlin) 30, 9, 441-446 (1978)

Various kinds of internal recycle reactors (Gradientless Laboreactor) published at this point of time are introduced.

2) Brown, C. E. et al.; A. I. Ch. E. J. 16 (5). 817-822 (1970)

A reaction rate of gas phase methanol synthesis is obtained by a self-made internal recycle reactor.

(4) Autoclave

As a technique similar to the internal recycle reactor, a method of evaluating a solid catalyst in a gas phase or a liquid phase by using an autoclave has been known by those skilled in the art for a long time.

However, in the Berty reactor mentioned in the above item (1), the reactor mentioned in the item 1) treats only a gas phase reaction system. Further, the method described in the item 2) has the following disadvantages.

(a) A solvent in a liquid phase is not successively discharged.

(b) Since the reactor is fully filled with the liquid, an interface area between the gas and the liquid is insufficient so that a mass transfer from the gas phase is liable to become a rate-determining.

(c) Since the reaction gas is introduced from a lower portion of a magnetic agitator, when the gas introduction rate is increased, there is a case that the impeller moves upward so as to come into contact with a catalyst basket, thereby leading to a breakage. The inventors have actually experienced the breakage of the impeller.

(d) Since a gaseous raw material and a solvent are respectively introduced into a reactor from separate inlets, in the event that the solvent is a heavy oil (for example, an atmospheric residual oil), there is a case that a coking is effected during a process of passing through the inlet portion of the reactor, thereby leading to a plugging. The inventors have actually experienced the plugging.

Further, in the Spinning basket reactor mentioned in the above item (2), the reactors described in the items 1) and 2) have the following disadvantages.

(a) Since the fluid is rotated together with the catalyst basket, an actual flow rate of the fluid with respect to the catalyst can not be evaluated.

(b) When the flow rate can not be evaluated, a mass transfer rate between the gas and the liquid or between the liquid and the solid becomes unclear, so that a intrinsic reaction rate can not be obtained.

(c) Since it is significantly difficult to fix a center of the basket when packing the basket with the catalyst, if the basket filled with the catalyst is rotated at a high speed, a bearing supporting a drive shaft is worn during a short period of time, so that it is not suitable for evaluating a catalyst for several months.

(d) In FIG. 3 of the reference "An Improved Gas Recirculation Reactor For Catalytic Studies", Caldwell, L.; Apply. Catal. 8. 199-213 (1983), it is pointed out that the spinning basket type (this is called as Carberry type in the reference) has less performance than the Berty type.

Further, in the other internal recycle reactors of fixed catalyst type mentioned in the above item (3), both of the reactors described in the items 1) and 2) do not disclose the applied reaction system.

Still further, the autoclave mentioned in the above item (4) mostly performs a screening test of the catalyst in a batch operation, so that it is impossible to obtain data having such a high accuracy as in a continuous operation. Further, although there is an example of evaluating by a continuous

operation in such a manner as not to change a liquid surface within the reactor in the same manner as the spinning basket, in the case that the catalyst is not fixed, since a diameter of a particle of the catalyst is changed during the reaction, a correctly evaluated result can not be obtained, and also in the case that the catalyst is fixed by using a cage or a net, since a chart for evaluating a rotating speed and a flow rate when the fluid passes through the catalyst layer as in the Berty reactor is not disclosed, the flow rate can not be evaluated as well.

As mentioned above, in all of the conventional evaluating apparatuses, in the case that a fluid to be evaluated is a liquid phase or a gas-liquid phase, since it is difficult to continuously discharge the evaluated fluid, the apparatus is exclusively used for a gas phase reaction system.

However, it has been strongly desired for a long time to enlarge a range of the fluid to be applied to a liquid phase or a gas-liquid phase in various kinds of technical fields in which it is necessary to use a solid catalyst and to perform various kinds of reactions in a liquid phase or a gas-liquid phase for the purpose of tests and researches.

Incidentally, as a method of evaluating a catalyst under a liquid phase and a gas-liquid phase in the Berty reactor, although the following two references disclose an information that an evaluation of a catalyst under a liquid phase and a gas-liquid phase can be performed, in any of these references, a concrete method thereof is not disclosed.

1) Ohta; Idemitsu Technical Report, 34 (4), 397-402 (1991)

2) 3" Catalytic reactors catalogue No.3821 autoclave engineer company

#### SUMMARY OF THE PRESENT INVENTION

The present invention is achieved by taking the above problems into consideration, and an object of the present invention is to provide an apparatus for evaluating a solid catalyst which enlarges a range of an applied fluid used for an evaluation of a performance of the solid catalyst and can accurately estimate the performance of the solid catalyst on a laboratory scale and a method of evaluating a solid catalyst using the apparatus.

In order to achieve the above object, according to the present invention, there is provided an apparatus for evaluating a solid catalyst comprising a raw material feeding portion for feeding a fluid raw material, a reacting portion having a reactor which brings the fed fluid raw material into contact with a solid catalyst disposed within the reactor so as to react therewith, and a recovering portion for recovering a reaction product fed from the reacting portion, wherein the raw material feeding portion has a function capable of continuously feeding a liquid raw material or a mixed raw material consisting of a gas and a liquid, wherein the reactor in the reacting portion has an inlet for the fluid raw material and reaction product outlets for discharging the reaction product while separating it respectively into a liquid product and a gaseous product, and wherein the recovering portion has reaction product inlets connected to each of the reaction product outlets of the reactor and has a liquid level control portion for keeping a liquid level within the reactor constant.

Further, as a preferred mode of the present invention, there is provided an apparatus for evaluating a solid catalyst, wherein the recovering portion has the reaction product inlets and the liquid level control portion and further has a gas-liquid separating portion for separating the reaction product fed from the liquid level control portion into a gas and a liquid.

Still further, as a preferred mode of the present invention, there is provided an apparatus for evaluating a solid catalyst,

wherein the reactor in the reacting portion is an internal recycle reactor of a fixed catalyst type.

Furthermore, as a preferred mode of the present invention, there is provided an apparatus for evaluating a solid catalyst, wherein the liquid level control portion is a control tank of an overflow type.

Moreover, according to the present invention, there is provided a method of evaluating a solid catalyst by using the apparatus for evaluating a solid catalyst, comprising a step of bringing the fluid raw material in the reacting portion into contact with the solid catalyst under a state of liquid phase or gas-liquid phase, and a step of continuously discharging the reaction product.

Further, as a preferred mode of the present invention, there is provided a method of evaluating a solid catalyst, wherein the fluid raw material is a group of oils or a mixed fluid of a group of oils and hydrogen.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an explanatory view which shows schematically an embodiment of an apparatus for evaluating a solid catalyst in accordance with the present invention;

FIG. 2 is an explanatory cross-sectional view which shows schematically an embodiment of an internal recycle reactor used in the present invention;

FIG. 3 is an explanatory view which shows a relation between  $1/LHSV$ , that is, a residence time and a conversion of desulfurization (X) in the evaluation of the catalyst in the present invention;

FIG. 4 is an explanatory view which shows Arrhenius plots of a first order reaction rate constant obtained in the evaluation of the catalyst in the present invention;

FIG. 5 is an explanatory view which shows relations between  $1/LHSV$ , that is, a residence time, a conversion of desulfurization (HDS) and a conversion of hydrocracking (HYC) in the evaluation of the catalyst in the present invention; and

FIG. 6 is an explanatory view which shows a comparison of evaluated results of the conversion of desulfurization (HDS) and the conversion of hydrocracking (HYC) in Example 2 and Comparison Example 3.

#### DESCRIPTION OF THE PREFERRED EMBODIMENT

An embodiment of the present invention will be concretely described below with reference to the drawings.

FIG. 1 is an explanatory view which shows schematically an embodiment of an apparatus for evaluating a solid catalyst in accordance with the present invention.

FIG. 2 is an explanatory cross-sectional view which shows an embodiment of an internal recycle reactor used in the present invention.

##### I. Apparatus for Evaluating a Solid Catalyst

As shown in FIG. 1, an apparatus for evaluating a solid catalyst in accordance with the present invention is mainly constituted by a raw material feeding portion 1, a reacting portion 2 and a recovering portion 3.

##### 1. Raw Material Feed Portion

As the raw material feeding portion 1 for feeding a fluid raw material, as far as it has a function of continuously feeding a liquid raw material or a mixed raw material of a gas and a liquid, there is no special limitation. For example, there is exemplified a raw material feeding portion which has a liquid raw material feeding portion and a gas raw

material feeding portion and which is capable of switching the fluid to be fed. By structuring in this manner, a fluid raw material to be fed to the next reacting portion 2 can be made into three kinds of a gas, a liquid and a gas-liquid mixture.

Here, as a liquid raw material fed from the liquid raw material feeding portion, for example, a group of oils or various kinds of solvents whose pressure is increased by a pump, etc. and whose flow rate is controlled by a flow meter, etc. can be exemplified. Even in the case of heavy oil such as atmospheric residual oil, etc., it can be used if a line is heated to a temperature at which it can keep fluidity.

Further, as a gas raw material fed from the gas raw material feeding portion, for example, a reaction gas such as a hydrogen or inert gas and the like whose pressure is increased to a reaction pressure by a compressor, a bomb, etc. and whose flow rate is controlled by a flow meter, etc. can be exemplified.

##### 2. Reacting portion

The reacting portion 2 in the present invention has a reactor 20 in which a fluid raw material fed from the raw material feeding portion 1 through a gas-liquid feeding tube 11 is contacted and reacted with a fixed catalyst 23 disposed in an inner portion thereof.

##### (1) Reactor

As the reactor 20 used in the present invention, for example, an internal recycle reactor shown in FIGS. 1 and 2 can be exemplified. As this reactor, a tank type-agitating reactor of the system of fixing the catalyst, which has a jacket or an electric furnace and can control a reaction temperature, is preferable. Among others, a Berty reactor is preferable. Further, it may be a reactor of the system of rotating the catalyst or an autoclave. In the embodiment shown in FIGS. 1 and 2, the fluid raw material flowing from a fluid raw material inlet 21 is made into a gas-liquid mixed phase by an agitator 26 and a constant flow (in this case, a downstream flow) of the gas-liquid is formed in layers of the fixed catalyst 23, and as shown in FIG. 2 it is contacted and reacted with the catalyst fixed to a catalyst packing bed 22. Among reaction products, a liquid product is discharged from an outlet 24 disposed, for example, in the lower portion and a gaseous product from an outlet 25, for example, disposed in an upper portion.

In the embodiment shown in FIG. 2, a body 50 of the reactor 20 is surrounded by a brass electric furnace 51 and a reaction temperature can be controlled. Further, a thermocouple inserting port 52 for inserting a thermocouple used for controlling a temperature of the fixed catalyst 23 is provided in the upper portion. Still further, the body 50 of the reactor is covered by a cover 55.

Here, as the fixed catalyst 23, for example, a fixed catalyst of a heterogeneous system can be exemplified. Concretely speaking, it is preferable to fill an alumina-supported catalyst, a zeolite catalyst, an activated carbon supported carrier catalyst and the like into a packing cylinder 57 fixed within the reactor 20. Further, it is preferable to provide a porous liquid dispersion plate 56 in an upper portion of the packing cylinder 57.

By providing the liquid dispersion plate 56, a maldistribution of the fluid raw material can be prevented, so that the raw material can be uniformly brought into contact with the fixed catalyst 23.

As the agitator 26, as far as it can agitate the fluid raw material within the reactor 20, there is no special limitation, however a magnetic agitator which can keep a pressure is preferable. In the embodiment shown in FIG. 2, it is constituted by a magnetic agitator shaft 53, an impeller 54 and a driving portion (not shown). The mounting direction may be either a vertical lower direction or a vertical upper direction.

A flow rate of the fluid raw material in the layer of the fixed catalyst 23 is controlled by a shape of the impeller 54 of the agitator 26, an adjustment of the rotating speed and the like.

Further, a liquid level of the fluid raw material within the packing cylinder 57 is preferably controlled so as to be constant by discharging the liquid raw material in correspondence to the feed thereof.

Incidentally, in the case that the fluid raw material is only the liquid raw material, the constitution shown in FIG. 2 may be used as it is, or the gaseous product outlet 25 may not be used. Further, the constitution having no gaseous product outlet may be used. In this case, the position in which the liquid product outlet 24 is disposed can be provided anywhere irrespective of whether it exists in the upper portion or lower portion of the reactor.

### 3. Recovering Portion

The recovering portion 3 in accordance with the present invention has, as shown in FIG. 1, a liquid level control portion 30 for keeping a liquid level within the reactor 20 constant and a gas-liquid separating portion 31 for separating the gas-liquid product fed from the control portion 30 into a gas and a liquid.

#### (1) Liquid Level Control Portion

The liquid level control portion 30 in the present invention communicates respectively with the liquid phase and the gas phase of the reaction product discharged from the reactor 20, thereby keeping the liquid level within the reactor 20 constant.

In the embodiment shown in FIG. 1, a (gas)-liquid feeding tube 32 and a gas introduction tube 33 for communicating the liquid product outlet 24 and the gaseous product outlet 25 provided in the reactor 20, respectively with a liquid product inlet 38 and with a gaseous product inlet 39 provided in the lower portion and in the upper portion.

As a liquid level control tank 34 corresponding to a body portion of the liquid level control portion 30, an overflow type shown in FIG. 1 is convenient and preferable.

By constituting in this manner, even in the case of switching and using only the reacting portion of the catalyst evaluating apparatus already provided, the liquid level can be kept constant without mounting a liquid level sensor or a liquid level control valve.

Incidentally, when a function of controlling the liquid level is given to the gas-liquid separating portion 31 disposed in the later step, which will be mentioned below, and the liquid level control portion can be disposed in a suitable position, that is, the position in which the liquid level of the gas-liquid separating portion 31 is higher than the upper end of the catalyst packing cylinder 57 within the reactor by a degree influenced by the discharge pressure (the fluid head) in the agitator 26, for example, in the case that a set of evaluating apparatus is newly provided, the control tank 34 may not be necessarily provided.

Further, in the case that the liquid product is heavy oil such as atmospheric residual oil and the like, it is preferable to heat the liquid product to a temperature at which it can keep a fluidity in the line.

#### (2) Gas-liquid separating portion

As the gas-liquid separating portion 31 used in the present invention, as far as the function of separating the reaction product into a gas and a liquid is possessed, there is no special limitation, and in the case that the liquid product is heavy oil such as atmospheric residual oil and the like, it is preferable to heat the liquid product to a temperature at which it can keep a fluidity in the line. In the embodiment shown in FIG. 1, the reaction product discharged from the

liquid level control tank 34 is introduced into a gas-liquid separating tank 35 through a gas-liquid feeding tube 36. It is preferable that a liquid level sensor 40 is disposed in the gas-liquid separating tank 35 and a liquid level control valve 58 is disposed the midway of a liquid feeding tube 41. Further, it is preferable that the gas-liquid separating tank 35 separates the reaction product from the gas-liquid feeding tube 36 into a gas and a liquid and a liquid level kept constant by the liquid level control valve 58. Still further, as a position of mounting the gas-liquid separating tank 35, it is suitable as far as the position is lower than a position of the liquid level control tank 34. Furthermore, as mentioned above, without the liquid level control tank 34, the gas-liquid separating tank 35 can be directly connected to the reactor 20. In this case, as an example, it is suitable that the gas introducing tube 33 and the gaseous product outlet line are connected to each other, and the gas-liquid feeding tube 32 and the gas-liquid feeding tube 36 are connected to each other. However, in this time it is necessary to set the position of mounting the gas-liquid separating tank 35 to a position higher than the upper end of the catalyst packing cylinder 57 within the reactor by a degree influenced by the discharging pressure (the fluid head) of the agitator 26.

#### (3) Evaluating Portion

The reaction product (the gaseous product and the liquid product) separated into a gas and a liquid in the gas-liquid separating tank 35 is introduced into the evaluating portion provided for the purpose of measuring the flow rate, analyzing the composition and so on through a pressure control valve 37 and a cooler (not shown in FIG. 1) respectively disposed in the later step, thereby evaluating the solid catalyst.

Also in this case, in the case that the liquid reacting material is heavy oil such as atmospheric residual oil and the like, it is suitable to heat the line to a temperature capable of keeping the fluidity.

### II. Method of Evaluating a Solid Catalyst

A procedure of a method of evaluating a solid catalyst in accordance with an embodiment of the present invention will be described below with reference to FIG. 1. Depending on a purpose of the evaluation, there is no need to necessarily accord with this procedure.

#### (1) Catalyst Packing

1) The catalyst 23 to be evaluated is packed within the reactor 20.

There is no special limitation on the packing amount of the catalyst and, for example, it can be set to be one particle to several m<sup>3</sup>. Although it depends on a volume of the reactor, it is preferable to set to a degree of 10 ml to 300 ml. When the packing amount is less than 10 ml, there is a risk that a maldistribution is caused, and when it exceeds 300 ml, there is a risk that the evaluating apparatus exceeds the laboratory scale, so that it becomes expensive.

2) The porous liquid dispersion plate 56 is disposed in the upper portion of the packing cylinder 57 in order to prevent the maldistribution.

3) The cover 55 of the reactor is closed.

#### (2) Leak Test

1) The pressure in the reactor 20 is increased to a level equal to or higher than a reaction pressure by using a suitable gas, thereby confirming that there is no leakage and no pressure reduction.

#### (3) Wetting

1) A predetermined amount of gaseous raw material is fed from the raw material feeding portion 1 in accordance with a desired evaluation condition.

2) The reaction temperature is increased in accordance with the desired evaluation condition.



3) A predetermined amount of liquid raw material is fed from the raw material feeding portion 1 in accordance with the desired evaluation condition.

4) It is recognized that the reactor 20 is filled with the liquid raw material, the catalyst is wetted, the liquid level control tank 34 becomes a predetermined liquid level and the gas-liquid separating tank 35 reaches a predetermined liquid level.

As a temperature at this time, it is preferable that it is a temperature equal to or higher than a temperature at which the liquid raw material flows and a temperature equal to or lower than a temperature at which the catalyst 23 does not react with the liquid raw material.

At a temperature lower than a flowing point there is a risk that the agitator 26 is broken, and at a temperature at which the reaction occurs, there is a risk that the reaction is excessively proceeded on the catalyst surface and thus the catalyst is deteriorated because the flowing has not started yet.

5) It is necessary to make the liquid level of the liquid level control tank 34 higher than the upper end of the catalyst packing cylinder 57 within the reactor by a degree influenced by the discharge pressure (the fluid head) in the agitator 26.

When the liquid level is low, the liquid raw material is not circulated or even when it is circulated, it is intermittently fed to the catalyst. Further, when the liquid level is high, the gas is not stored in the upper portion of the reactor, so that a gas-liquid interface area is largely reduced.

6) After confirming the above item 4), the agitator 26 is rotated in accordance with the desired evaluating condition and the liquid raw material is brought into contact with the solid catalyst under a state of a liquid phase flow or a gas-liquid two phase flow.

#### (4) Pre-Treatment of the Catalyst

1) In accordance with the desired evaluating condition, a pre-treatment of the catalyst is performed. As the pre-treatment, there are, for example, a catalytic reduction, a catalytic pre-sulfurization and the like. On the basis of the characteristic of the tank reactor, considering the fact that the reaction efficiency thereof is lower than that of the tubular type, it is preferable to select a condition which is somewhat more excessive than the tubular reactor.

For example, there are exemplified that a temperature for the pre-treatment temperature is made high, a time for the pre-treatment is made long, a raw material for the pre-treatment is fed somewhat in a large amount, and so forth.

#### (5) Evaluation of Reaction

1) The reaction product is continuously discharged from the recovering portion 3 and an evaluation of the catalyst is performed in accordance with the desired evaluating condition.

#### (6) Shut Down of the Apparatus

1) When the evaluation of reaction is completed, the reaction temperature is decreased.

2) If necessary, the liquid raw material is replaced by a detergent.

3) When the temperature is decreased to a safety temperature, the feed of the liquid raw material is stopped.

4) The gaseous raw material is replaced by an inert gas, etc. and the inner portion of the reacting apparatus is substituted.

5) The rotation is stopped and the pressure is extracted.

Incidentally, since in most of the internal recycle reactors, the gas is not circulated under a atmospheric pressure (when the specific gravity of the gas is low, the agitating effect becomes low and so the internal circulation does not occur), it is preferable to perform the pressure extraction at the last time.

#### (7) Analysis of the Reaction Results

1) The results of evaluating the catalyst in the internal recycle reactor are analyzed as the tank type (a continuous stirred tank reactor).

2) A reaction rate constant is obtained by a suitable order of reaction and its conversion to the tubular type is performed.

The present invention will be further concretely described below with reference to Examples.

#### EXAMPLE 1

##### (Evaluating Apparatus)

The catalyst is evaluated on the basis of the evaluating apparatus having a constitution shown in FIG. 1. The main constitutional elements used are as follows.

Internal recycle reactor: The one in which a modification is added to 3 inches Berty reactor manufactured by AUTO-CLAVE ENGINEER COMPANY in such a manner as shown in FIG. 2.

Catalyst to be evaluated: Heavy oil hydrocracking catalyst A (Co—Mo system/Alumina+USY, 1/16 inches trilobed type) 15, 50 ml packing

Raw material oil: Dibenzothiophene+n-tridecane (both are special grade test reagents) is prepared to have a sulfur concentration of 0.3 weight percents.

##### (Pre-Treatment of the Catalyst)

In the pre-treatment of the catalyst, a pre-sulfurization is performed under the following conditions.

Sulfurization agent: non-desulfurized light gas oil having a sulfur concentration of 1.16 weight percents and the specific gravity of 0.8430

Pressure: 115 kg/cm<sup>2</sup>G

Sulfurization temperature: 260 ° C.

LHSV: 1.0 1/h

Sulfurization time: 24 hours

Hydrogen/oil ratio: 1000 Nm<sup>3</sup>/kl

##### (Reaction Condition)

The reaction in the reactor is performed under the following conditions.

Pressure: 100 kg/cm<sup>2</sup>G

Reaction temperature: 200 to 300° C.

LHSV: 1 to 10 1/h

Hydrogen/oil ratio: 2000 Nm<sup>3</sup>/kl

Rotating speed of agitator: 1000 rpm

Estimating value of superficial liquid linear speed: 6 cm/s (when a packing amount of the catalyst is 50 ml) and 11 cm/s (when a packing amount of the catalyst is 15 ml)

##### (Evaluation Results)

The conversion of desulfuration is obtained from a sulfur concentration at the inlet and the outlet of the reactor.

FIG. 3 shows a relation between 1/LHSV (that is, a residence time) and the conversion of desulfuration (X).

As shown in FIG. 3, it is understood that the conversion of desulfuration (X) is dependent on a first order reaction rate of the tank reactor over a wide range of the LHSV.

First order reaction rate equation of the tank reactor:

$$k = \text{LHSV} \times X / (1 - X) \quad (1)$$

First order reaction equation of the tubular reactor:

$$k = \text{LHSV} \times \{-1/\ln(1 - X)\} \quad (2)$$

The reaction rate constant k is obtained by the above equation (1).

FIG. 4 shows Arrhenius plots of the obtained first order reaction rate constants.

The drawing shows a linear relation and  $E_a = 25.7$  kcal/mol is obtained as an activation energy.

As mentioned above, from the fact that the conversion of desulfuration is dependent on the first order reaction rate equation, that the Arrhenius plots become linear and that the activation energy becomes a value showing a reaction rate-determining, it is understood that this evaluating method gives appropriate results.

#### Comparison Example 1

##### (Evaluating Apparatus)

Under a state that in the reactor of Example 1, the internal recycle reactor is replaced by an isothermal tubular reactor, the evaluation is performed by the following structure.

Isothermal tubular reactor: A tube type having a thermowell of an outer diameter of 6.35 mm in the center portion and having an inner diameter of 19 mm and a length of 1.2 m

Catalyst to be evaluated: The same catalyst A as Example 1 is packed in an amount of 50 ml.

Raw material oil: The same as Example 1

##### (Pre-Treatment of the Catalyst)

In the pre-treatment of the catalyst, a pre-sulfurization is performed under the following conditions.

Pressure: 135 kg/cm<sup>2</sup>G

The other conditions are the same as Example 1.

##### (Reaction Condition)

The reaction in the reactor is performed under the following conditions.

Reaction temperature: 275 ° C.

LHSV: 1 to 3 1/h

Superficial liquid linear velocity: 2E-3 cm/s (when the LHSV =1) and 6E-3 cm/s (when the LHSV =3)

Pressure and hydrogen/oil ratios are the same as Example 1.

##### (Evaluation Results)

Table 2 shows a comparison between Example 1 and Comparison example 1 in terms of the evaluation results (X=a conversion of desulfuration [%] of dibenzothiophene in n-tridecane). The evaluation results of Example 1 in Table 2 is the one converted into the conversion of desulfuration in the tubular type by the first order reaction rate equation (2) of the tubular type from the obtained speed constant.

In Comparison example 1, since in the tubular reactor the superficial liquid linear speed is lower than one thousandth in comparison with Example 1, it is understood that a correct reaction result can not be obtained due to the influence of the material movement.

#### Comparison Example 2

Except the fact that, in Comparison Example 1, as a catalyst to be evaluated in the isothermal tubular reactor the one mentioned below is used and the flow is improved by packing a catalyst diluted with fine particles, the evaluation is performed in the same manner as Comparison Example 1.

Catalyst to be evaluated: The same catalyst A as Example 1 in an amount of 50 ml and 32-64 mesh silicon carbide in an amount of 50 ml are alternately packed little by little.

##### (Evaluation Results)

Table 2 shows comparison & between Example 1, Comparison example 1 and the Comparison example 2.

In the Comparison example 2, although it is recognized that the conversion of desulfuration is slightly improved in Comparison with the comparison example 1 due to the effect that the catalyst is diluted with the fine particles (this effect mainly suppresses an influence of an back mixing), the desulfuration rate is significantly lower in comparison with Example 1, so that it is understood that there is a limitation in the tubular reactor in comparison with the internal recycle type.

TABLE 2

LHSV (1/h)	Example 1	Comparison Example 1	Comparison Example 2
1.0	99.9	90.9	96.8
1.5	99.3	83.3	90.8
2.0	97.6	80.3	84.8
3.0	91.8	70.0	73.0

Note: Example 1 shows results obtained by of estimating into a conversion of desulfuration in the tubular type from a reaction rate constant of the tank type.

#### EXAMPLE 2

##### (Evaluating Apparatus)

Except that heavy oil mentioned below is used instead of the raw material in Example 1, the same apparatus as Example 1 is used. However, the catalyst to be evaluated is packed in an amount of 50 ml.

Raw material oil: Atmospheric residual oil of Arabian heavy crude oil (the characteristic thereof is shown in Table 3)

##### (Pre-Treatment of the Catalyst)

In the pre-treatment of the catalyst, a pre-sulfurization is performed under the following conditions.

Sulfurization agent: non-desulfurized light gas oil having a sulfur concentration of 1.16 weight percents and the specific gravity of 0.8430

Pressure: 130 kg/cm<sup>2</sup>G

Sulfurization temperature: 250 ° C.

LHSV: 1.0 1/h

Sulfurization time: 24 hours

Hydrogen/oil ratio: 1000 Nm<sup>3</sup>/kl

##### (Reaction Condition)

The reaction in the reactor is performed under the following conditions.

Pressure: 130 kg/cm<sup>2</sup>G

Reaction temperature: 380 °C

LHSV: 0.3 to 1.0 1/h

Hydrogen/oil ratio: 700 Nm<sup>3</sup>/kl

Rotating speed of agitator: 1000 rpm

Estimating value of superficial liquid linear velocity: 4 cm/s

##### (Evaluation Results)

The conversion of desulfuration and the conversion of hydrocracking are obtained from the sulfur concentration at the outlet and the inlet of the reactor and from the weight content of fraction having a temperature equal to or higher than 343° C. and measured by a distillation gas chromatography.

FIG. 5 shows relations between 1/LHSV (that is, a residence time), the conversion of desulfuration (HDS) and the conversion of hydrocracking (HYC). According to FIG. 5, it is understood that the HDS and the HYC are dependent on the first order reaction rate equation of the tank reactor over a wide range of the LHSV, and so it is understood that this evaluating method can give appropriate results also in the reaction of the heavy oil.

TABLE 3

Specific gravity (-)	0.9798
Kinematic viscosity @ 50° C. (cSt)	1098
Sulfur content (wt. %)	4.13
Nitrogen content (ppm)	2500

TABLE 3-continued

V content (ppm)	85
Ni content (ppm)	26
Micro residual carbon content (wt. %)	14.7
n-Heptane insoluble content (wt. %)	7.67

## Comparison Example 3

## (Evaluating Apparatus)

Except that the reactor used in Example 2 is replaced by an isothermal tubular reactor mentioned below is used, the same apparatus as Example 2 is used.

Isothermal tubular reactor: A tube type having a thermowell of an outer diameter of 7.94 mm in the center portion and having an inner diameter of 25 mm and a length of 3.5 m

Catalyst to be evaluated: The same catalyst A as Example 1 is filled in an amount of 700 ml.

Raw material oil: The same as Example 2

## (Pre-Treatment of the Catalyst)

In the pre-treatment of the catalyst, a pre-sulfurization is performed under the following conditions.

LHSV: 0.8 1/h

The other conditions are the same as those of Example 2.

## (Reaction Condition)

The reaction in the reactor is performed under the following conditions.

Reaction temperature: 380 ° C.

LHSV: 0.3 1/h

Superficial liquid linear velocity: 0.02 cm/s

Pressure and hydrogen/oil ratios are the same as Example 1.

## (Evaluation Results)

FIG. 6 shows a comparison in terms of results of evaluating the HDS and the HYC with Example 2. The evaluation result of Example 2 in FIG. 6 is the one estimated the HDS and the HYC in the tubular type by the first order reaction rate equation

(2) of the tubular type from the rate constant obtained by the tank type.

The results of evaluating the HDS and the HYC in Example 2 and Comparison Example 3 substantially agree with each other, and it is considered that both become in the same result because in the tubular reactor the superficial liquid linear velocity in the tubular reactor is equal to or less than one two hundreds and fiftieth in comparison with Example 2 but the reaction rate is lower in comparison with Example 1 and the like.

As mentioned above, in the desulfuration reaction and the hydrocracking reaction of the atmospheric residual oil, it is understood that the evaluating method in accordance with the present invention and the isothermal tubular reactor of the relatively large size both give an appropriate result, so that it is shown that the evaluating method in accordance with the present invention not only gives an appropriate result but also is useful for scale-up of a plant.

As described above, according to the present invention, there are provided an apparatus of evaluating the solid catalyst and a method for evaluating the solid catalyst, in which the range of the applied fluid used for evaluating the performance of the solid catalyst is enlarged from the gas phase to the liquid phase or the gas-liquid phase and the performance of the solid catalyst can be accurately evaluated by a small scale laboratory apparatus.

Further, according to the present invention, in developing a new plant, a step of a large size experimental apparatus (a demo plant, a pilot plant or the like) can be omitted.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from spirit and scope thereof.

What is claimed is:

1. An apparatus comprising

a raw material feeding portion for feeding a fluid raw material;

a reacting portion having a reactor for catalytically converting the fluid raw material into a reaction product, the reactor including a means disposed within the reactor for circulating the fluid raw material and a portion of the reaction product inside the reactor into contact with a fixed catalyst disposed within the reactor; and

a recovering portion for recovering a portion of the reaction product fed from the reacting portion, wherein

the raw material feeding portion has a function capable of continuously feeding a liquid raw material or a mixed raw material consisting of a gas and a liquid,

the reactor in the reacting portion has an inlet for the fluid raw material and reaction product outlets for discharging the reaction product while separating it respectively into a liquid product and a gaseous product,

the recovering portion has reaction product inlets connected to each of the reaction product outlets of the reactor and has a liquid level control portion for keeping a liquid level within the reactor constant.

2. The apparatus according to claim 1, wherein the recovering portion further comprises a gas-liquid separating portion for separating a reaction product fed out from the liquid level control portion into a gas and a liquid.

3. The apparatus according to claims 1 or 2, wherein the reactor in the reacting portion is a fixed catalyst internal recycle reactor.

4. The apparatus according to claims 1 or 2, wherein the liquid level control portion is an overflow control tank.

5. The apparatus according to claim 1, wherein the means for circulating is a fluid impeller.

6. The apparatus according to claim 1, wherein the fixed catalyst is disposed in a single catalyst bed within the reactor.

7. The apparatus of claim 6, wherein the reactor is a fixed catalyst internal recycle reactor.

8. The apparatus of claim 6, wherein the fixed catalyst is disposed in a single catalyst bed within the reactor.

9. A method of evaluating a solid catalyst, the method comprising

providing the apparatus of claims 1 or 2,

bringing a fluid raw material into the reacting portion of the apparatus and into contact with a fixed catalyst, and continuously discharging a reaction product.

10. The method according to claim 5, wherein the fluid raw material comprises at least one of the group consisting of oils and hydrogen.

11. An apparatus comprising

a raw material feeding portion;

**15**

a reacting portion connected to the raw material feeding portion; and

a recovering portion connected to the reacting portion, wherein

the reacting portion comprises a reactor including a fluid impeller disposed within the reactor and a fixed catalyst disposed within the reactor;

5

**16**

the reactor comprises a liquid product outlet and a gaseous product outlet; and

the recovering portion comprises a liquid product inlet connected to the liquid product outlet of the reactor, a gaseous product inlet connected to the gaseous product outlet of the reactor, and a liquid level control portion for keeping a liquid level within the reactor constant.

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